22
2-1-90 JS (2)

NIPER-452 (Vol. 1)
(DE90000200)

ANALYSIS OF HEAVY OILS: METHOD DEVELOPMENT
AND APPLICATION TO CERRO NEGRO HEAVY PETROLEUM

FINAL REPORT

DO NOT MICROFILM
COVER

December 1989

Performed Under Cooperative Agreement No. FC22-83FE60149

IIT Research Institute
National Institute for Petroleum and Energy Research
Bartlesville, Oklahoma

Bartlesville Project Office
U. S. DEPARTMENT OF ENERGY
Bartlesville, Oklahoma

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office Of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615)576-8401, FTS 626-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161

Price: Printed A23
Microfiche A01

CHAPTER 1

**DO NOT MICROFILM
THIS PAGE**

NIPER--452-Vol.1

DE90 000200

NIPER-452 (Vol. 1)

Distribution Category UC-125

ANALYSIS OF HEAVY OILS: METHOD DEVELOPMENT AND
APPLICATION TO CERRO NEGRO HEAVY PETROLEUM

FINAL REPORT

December 1989

Work Performed Under Cooperative Agreement No. FC22-83FE60149

Prepared for
U.S. Department of Energy
Assistant Secretary for Fossil Energy

W. D. Peters, Project Manager
Bartlesville Project Office
P.O. Box 1398
Bartlesville, OK 74005

Prepared by
IIT Research Institute
National Institute for Petroleum and Energy Research
Box 2128
Bartlesville, OK 74005

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DO NOT MICROFILM
THIS PAGE

(This page intentionally left blank.)

Q101

NOTICE

These two volumes contain the results of an eight year analytical research program that was undertaken to develop new methods for and new knowledge from the characterization of heavy petroleum. The title of the program is "Analysis of Heavy Oils: Method Development and Application to Cerro Negro Heavy Petroleum." While Cerro Negro, an eastern Venezuelan (Monagas) heavy oil, was the primary test material, other heavy oils were also used. To expedite dissemination of the results of this research, the individual chapters contained herein were initially published as a series of topical reports. They are reprinted here in their original form, except for correction of minor errors discovered after the original printing. These two volumes contain seven major reports, and associated appendices, and are issued as a unit for the convenience of the reader.

AUTHOR PAGE

ANALYSIS OF HEAVY OILS: METHOD DEVELOPMENT AND
APPLICATION TO CERRO NEGRO HEAVY PETROLEUM

by

J. A. Green
J. B. Green
R. D. Grigsby
C. D. Pearson
J. W. Reynolds
J. Y. Shay
G. P. Sturm, Jr.
J. S. Thomson
J. W. Vogh
R. P. Vrana
S. K.-T. Yu

NIPER Bartlesville, OK

B. H. Diehl
P. L. Grizzle
D. E. Hirsch
K. W. Hornung
S.-Y. Tang

Formerly of NIPER or U.S. Department of Energy

L. Carbognani
M. Ilazos
V. Sanchez

INTEVEP Caracas, Venezuela

ACKNOWLEDGMENT

The authors thank the U.S. Department of Energy and INTEVEP for financial support throughout this project. Also, the administrative and technical contributions of R. P. Anderson and W. D. Good of NIPER, W. D. Peters and S. E. Scheppele of the Bartlesville Project Office, U.S. DOE, and Alejandro Izquierdo of INTEVEP, S.A., were essential to the success of the overall project and this report. Finally, the assistance of Ms. Joan Haimson and the NIPER drafting department in manuscript preparation is greatly appreciated.

FOREWORD

On March 6, 1980, the U.S. Department of Energy (DOE) and the Ministry of Energy and Mines of Venezuela (MEMV) entered into a joint agreement which included analysis of heavy crude oils from the Venezuelan Orinoco oil belt. The objectives of the work on the Orinoco crudes were to: 1) provide detailed characterization of these crude oils, 2) develop new analytical methods for analyzing these and similar heavy oils, and 3) relate heavy oil composition to processes applicable to heavy oils in an effort to improve these processes and/or develop new processing methods. Specific tasks in the agreement included: 1) exchanges of existing information on the Orinoco crudes as well as available methods for their analysis, 2) exchanges of scientists from the respective organizations, 3) a coordinated research effort on analysis of one or more crude oils, and 4) exchanges of reports on both the results of analysis and new analytical methods developed during the project.

The purpose of this report is to present compositional data and describe new analytical methods obtained from work on the Cerro Negro Orinoco belt crude oil since 1980. Because of the Cerro Negro crude's compositional complexity, many new analytical methods and/or approaches were needed; thus, the bulk of the effort was actually spent on analytical method development rather than obtaining compositional data, per se. Most of the chapters focus on the methods rather than the resulting data on Cerro Negro oil, and results from other oils obtained during the verification of the method are included. In addition, published work on analysis of heavy oils, tar sand bitumens, and like materials is reviewed, and the overall state of the art in analytical methodology for heavy fossil liquids is assessed.

The geology and geochemistry of the Orinoco heavy oil deposits have been discussed previously (F-1,F-2)* and are not addressed further here. Cerro Negro can be classified as a type III heavy crude oil, using the classification scheme of Bestougeff, et al. (F-3). Other well known crudes in this classification include Boscan (western Venezuela) and Athabasca as well as most other Canadian tar sand bitumens. Type III heavy crude oils exhibit

*Underlined numbers in parentheses refer to items in the list of references at the end of this foreword.

densities (20° C) near or exceeding 1.000, extremely high viscosities (up to 8×10^6 cSt), and contain high levels of sulfur (up to 7 weight percent), asphaltenes (ca. 20 weight percent), and metals (Ni + V = 200 to 1300 ppm W/W) (F-3). These crudes represent the least desirable petroleum refinery feedstocks available. However, their great abundance worldwide (2.1×10^{12} bbl) (F-2) coupled with shrinking supplies of conventional crudes will steadily improve their economic viability and ultimately will require their commercial development as a matter of practical necessity. In order to achieve the commercial use of heavy crudes, significant improvements in refining technology for their upgrading will be needed (F-4). Furthermore, development of better processes will require the ability to analyze effectively and characterize both feed and resulting products from heavy oils. Thus, this need for better analytical methods to support process development for heavy oil upgrading formed the basis for the work described in this report.

The various phases of the work included: distillation and determination of "routine" physical/chemical properties (Chapter 1); preliminary separation of >200° C distillates and the residue into acid, base, neutral, saturated hydrocarbon and neutral-aromatic concentrates (Chapter 2); further separation of acid, base, and neutral concentrates into subtypes (Chapters 3-5); and determination of the distribution of metal-containing compounds in all fractions (Chapter 6).

The work was carried out by over twenty scientists, including three visiting scientists from the Instituto Tecnológico Venezolano del Petróleo (INTEVEP), at the Bartlesville, OK, DOE-owned facility. Approximately 20 man-years have been expended on the project to date. Nevertheless, the analysis of Cerro Negro heavy oil remains substantially incomplete; this point will become quite evident to those patient enough to read through this volume.

In general, problems in heavy oil analysis stem from their tremendous compositional complexity; a much higher heteroatom content and a much larger proportion of nondistillable material than conventional crudes; and, most importantly, lack of prior experience useful for focusing the analysis toward determination of the most significant compositional parameters needed for developing improved methods for producing, refining, and utilizing the heavy crudes. One result of these problems is the common practice of using very

simple parameters, such as a decrease in asphaltene content, as a measure of conversion in process development work with heavy oils. Although the inadequacy of bulk parameters in such applications is recognized (F-5), more detailed separation and analyses do not as yet provide a practical alternative because of their high cost, slow turnaround, and, most significantly, lack of proven track records for providing more useful results than the simpler bulk property tests.

Given the virtual impossibility of performing comprehensive analyses of heavy oils in order to predict methods for optimum production and refining, future work should be directed more toward identifying key compositional parameters. However, in order to pursue the most important aspects of heavy oil composition, a solid background in general heavy oil composition as well as a well-stocked arsenal of separation and instrumental methods will be needed. The work described in this report, in conjunction with contributions by other research groups over the same time, constitutes a significant step towards an improved understanding of heavy oil composition and methods suitable for their analysis.

REFERENCES

- F-1. Alayeto, E. M. B., and L. W. Louder. Canadian Soc. Petrol. Geol. Mem. 3, 1974, pp. 1-18.
- F-2. Demaison, G. J. Bull. Am. Assoc. Petrol. Geol., v. 61, 1977, p. 1950.
- F-3. Bestougeff, M., P. F. Burollet, and R. J. Byramjee. The Future of Heavy Crude and Tar Sands, Second International Conference, edited by R. F. Meyer, J. C. Wynn, and J. C. Olson. McGraw-Hill, New York, NY, 1984, pp. 12-16.
- F-4. Wells, J. W., and R. P. Anderson. Research Needs for Heavy Crude Processing and Utilization. Topical Report NIPER-187, 1986, 36 pp.
- F-5. Dolbear, G. E., A. Tang, and E. L. Moorehead. Fuel, v. 66, 1987, p. 267.

TABLE OF CONTENTS

<u>Chapter</u>	<u>NIPER No.</u>	<u>Title</u>	<u>Volume</u>
1	160	Analysis of Heavy Oils: Method Development and Application to Cerro Negro Heavy Petroleum. Distillation and Determination of Routine Chemical/Physical Properties	1
2	161	Analysis of Heavy Oils: Method Development and Application to Cerro Negro Heavy Petroleum. Preliminary Separation and Analysis of Acid, Base, and Aromatic Fractions	1
3	322	Analysis of Heavy Oils: Method Development and Application to Cerro Negro Heavy Petroleum. Detailed Separation and Analysis of Acidic Compounds	1
4	323	Analysis of Heavy Oils: Method Development and Application to Cerro Negro Heavy Petroleum. Detailed Separation and Analysis of Basic Compounds	2
5A	324	Analysis of Heavy Oils: Method Development and Application to Cerro Negro Heavy Petroleum. Detailed Separation and Analysis of Aromatic Hydrocarbons	2
5B	325	Analysis of Heavy Oils: Method Development and Application to Cerro Negro Heavy Petroleum. Detailed Separation and Analysis of Sulfur Compounds	2
6	289	Analysis of Heavy Oils: Method Development and Application to Cerro Negro Heavy Petroleum. Distribution of Metalloorganic Species in Acid-Base-Neutral Fractions of Cerro Negro 550-700° C Distillate and 700° C+ Residue	2

EXECUTIVE SUMMARY

The primary objective of the project was to determine the composition of Cerro Negro and other heavy (low API gravity) crude oils.

Initially, existing analytical methodology for separation and analysis of conventional and heavy petroleums was evaluated through its application to Cerro Negro and other petroleums, as well as coal-derived syncrudes. Although selected methods and/or elements of methods performed well toward their given task, the need for an integrated scheme for systematic separation and analysis of very complex materials like Cerro Negro became apparent even in the early phases of the work.

Thus, a major portion of the project became development of such a scheme. Figure 1 shows the resulting sequence of separation and analysis steps developed. Because of its general applicability and documented performance on Cerro Negro and other crudes, the methodology depicted in the figure (described in detail in the accompanying chapters) represents the most significant product from the research. While some elements of the scheme consist of conventional techniques (e.g., distillation), others encompass significantly improved versions of earlier methods (e.g., nonaqueous ion exchange LC) or novel procedures (e.g., schemes 1-4).

Application of the analytical scheme to Cerro Negro and other crudes led to the following general findings.

- The average molecular weight ($\overline{MW}$) of Cerro Negro crude (638) is clearly greater than that of conventional crudes, but only by a factor of 2 or 3. Cerro Negro resid has a $\overline{MW}$ comparable to those from other crudes (≤ 996); thus, the higher overall $\overline{MW}$ for the crude simply results from its lower distillate content.

CHEMICAL/PHYSICAL SEPARATIONS

ANALYSIS

FIGURE 1. Schematic for separation and analysis of conventional, heavy, or synthetic crudes and their products.

- The presence of significant quantities of distinct macromolecules with $\overline{MW}$ of several thousand in heavy petroleum is an improbable concept which largely originated from erroneous $\overline{MW}$ estimates obtained under conditions promoting intermolecular association. Similarly, commonly observed phenomena such as asphaltene precipitation, abnormally high viscosities or specific gravities for certain oils, and the presence of apparently distillable materials in nondistillable fractions all reflect effects of intermolecular association rather than the presence of large macromolecules.
- Although acid-base or other types of pairing could account for relatively small increases in apparent $\overline{MW}$, the extensive association indicated by measurements on resid fractions is totally inconsistent with a functional group-based association mechanism. The available evidence supports charge-transfer or an analogous type of bonding between aromatic systems as the dominant intermolecular association mechanism. For example, significant association between neutral aromatic compounds occurred, especially in the absence of saturated hydrocarbons. Thus, heteroatoms and metals increase association indirectly by enhancing charge-transfer between aromatic moieties rather than through direct coupling.
- The composition of Cerro Negro differs from that of conventional petroleums in many respects. In addition to obvious features like lower distillate and higher heteroatom (including metals) content, Cerro Negro was found to contain virtually no straight-chain or isoparaffins; saturated hydrocarbons are almost entirely of naphthenic type. The majority of neutral-aromatic compounds contain sulfur in sulfide or thiophenic forms, or other heteroatoms in functional groups exhibiting low polarities; aromatic hydrocarbons comprise less than one-half of the total neutral-aromatic fractions from all boiling ranges $>425^\circ \text{C}$. For acidic and basic compounds, the number of heteroatoms and functional groups per molecule exceeds one for all boiling ranges investigated; e.g., the average empirical formula for $200\text{--}425^\circ \text{C}$ bases is $\text{C}_{19.8}\text{H}_{28.6}\text{N}_{0.86}\text{O}_{0.58}\text{S}_{0.26}$ ($\text{N}+\text{O}+\text{S} = 1.7$), and for $>700^\circ \text{C}$ bases, $\text{C}_{81.1}\text{H}_{100.5}\text{N}_{1.35}\text{O}_{0.87}\text{S}_{1.75}\text{Ni}_{0.006}\text{V}_{0.03}$ ($\text{N}+\text{O}+\text{S} = 4.0$).

- Because of their significant differences in composition, correlations and models developed for predicting chemical composition and behavior, as well as physical properties of conventional petroleum will generally not hold for Cerro Negro and like materials. For example, the ASTM mass spectrometric method D 2786 for analysis of saturated hydrocarbons yielded inaccurate results for Cerro Negro because it employs data reduction procedures based on n- or isoparaffin matrices.
- The compositional complexity of Cerro Negro virtually defies comprehension. Individual compounds determined in distillate fractions typically accounted for only 0.1 to 1 ppm of a given distillate. Thus, for the 200-425° C boiling range (22.42 wt % of the whole crude), the total number of compounds present almost surely exceeds 10^5 --to an upper limit of 10^7 - 10^8 . Moreover, compositional complexity clearly increased with boiling point. Given the above, description of its composition at the individual compound level clearly exceeds any practical limits for available manpower, time, or funds.
- Structural variation within each chemical class or type generally prevented isolation of fractions containing a single class, or a given class into a single fraction. Steric factors, effects from neighboring groups or heteroatoms, and intramolecular bonding affected separation behavior and other physical/chemical properties of acidic and basic compound classes to the extent that subclassification was justified in many cases (e.g., "normal," hindered, hydrogen-bonded, sulfur-containing, etc., hydroxyaromatic compounds).
- Especially in the case of the distillation residue, chemical separation behavior reflected the complete molecular structure of a given compound and was generally not controlled by a particular heteroatom or entity. Thus, except for the saturated hydrocarbon fraction, all chromatographic fractions obtained from the residue (see

figure 1) generally contained significant proportions of the total N, O, S, Ni, and V present. In light of this result, selective extraction or adsorption of particularly deleterious elements such as Ni or V from the neat crude or residue does not appear to be technically feasible.

Recommendations

One of the many pitfalls in heavy oil analysis is that, out of the nearly endless number of parameters which could be measured, most merely indicate additional negative aspects of the oil's composition or do not significantly build on information available from standard inspection tests. For example, the popular approach in analysis of conventional, sweet, crudes was identification of minor levels of "bad actor" compounds containing heteroatoms and/or exhibiting a high degree of aromaticity which might cause problems during refining. In the case of Cerro Negro, the latter phrase describes the majority of compounds in the crude! Separations reported in the literature for isolation and quantification of generic compound types, e.g., nitrogen compounds, often yield essentially the same information attainable from distillation combined with elemental analysis. Future analytical research on heavy oils should focus on determination of parameters unobtainable by current methods, and of direct relevance to ongoing production and process development research.

Until very detailed or unconventional compositional information can be generally employed in practical correlations, it will remain in the realm of academic interest. Because of their greater complexity and obscurity, such correlations are much harder to come by than those based on simpler parameters. For example, total sulfur or total metals have direct application in refinery processes because their ultimate fate is known and their upper limit in products is specified. On the other hand, a parameter such as the concentration of a specific homologous series, e.g., alkylbenzo[c]carbazoles, receives only a passing glance because its impact cannot be assessed within the current state of the art. A tremendous effort would be needed in order to generally be able to translate such specific chemical information to practical effects on physical properties or refinery product state. Without the commitment to obtain such correlations, continued analysis of heavy oils is of limited value.

The separation scheme presented here could serve as a starting point for expanding existing knowledge of the impact of individual compound classes, types, or psuedo-types on heavy oil properties and chemical behavior. For example, use of chromatographic fractions during investigation of inter-molecular association is discussed in Chapter 1, part B. Use of actual heavy oil fractions as screening tools to determine relative importance of the myriad of compounds present is a reasonable starting point towards deriving correlations discussed in the preceding paragraph.

In terms of published papers, the most active area for analytical research in petroleum is currently developing methods/approaches to obtain inspection-type parameters in less time and at lower cost. Recent examples include a near-infrared method for determining octane number and other properties of gasoline, and supercritical fluid or high temperature gas chromatographic methods for simulated distillation of whole crudes. The main driving forces behind this work are the desires of instrument manufacturers to sell new instruments and of petroleum lab managers to increase productivity in order to offset stagnant or decreasing budgets and manpower limits. Without slighting either of the above goals, it should be recognized that this type of work does not address the long-term technological needs for the inevitable transition from conventional to heavy oil.

Whether or not the work performed or recommended herein addresses technological needs for utilization of heavy oil is open to conjecture; however, the existence of those needs is unequivocal, considering both the differences between its composition versus conventional petroleum and the increasing environmental and product quality constraints on the industry as a whole.

**ANALYSIS OF HEAVY OILS: METHOD DEVELOPMENT AND
APPLICATION TO CERRO NEGRO HEAVY PETROLEUM**

**Distillation and Determination of Routine
Chemical/Physical Properties**

Topical Report

**By
J.B. Green
P.L. Grizzle
J.S. Thomson
J.Y. Shay
B.H. Diehl
K.W. Hornung
V. Sanchez**

October 1988

Work Performed Under Cooperative Agreement No. FC22-83FE60149

**Prepared for
U.S. Department of Energy
Assistant Secretary for Fossil Energy**

**W.D. Peters, Project Manager
Bartlesville Project Office
P.O. Box 1398
Bartlesville, OK 74005**

**Prepared by
IIT Research Institute
NATIONAL INSTITUTE FOR PETROLEUM AND ENERGY RESEARCH
P.O. Box 2128
Bartlesville, OK 74005**

**DO NOT MICROFILM
THIS PAGE**

(This page intentionally left blank.)

TABLE OF CONTENTS

	<u>Page</u>
Foreword.....	iii
Abstract.....	ix
Acknowledgments.....	ix
Part A. Distillation and Determination of Routine Chemical/Physical Properties.....	1
Introduction, Part A.....	1
Experimental, Part A.....	3
Distillations.....	3
GC-Simulated Distillations.....	3
Small Scale Pot-Type Distillations.....	5
Large-Scale Wiped-Wall Distillation.....	6
Determination of Physical/Chemical Properties.....	6
Results, Part A.....	9
Distillations.....	9
Physical/Chemical Properties.....	25
Discussion, Part A.....	28
Distillation.....	28
Chemical/Physical Properties of Heavy Crudes.....	30
Summary and Conclusions, Part A.....	34
Part B. Determination of Average Molecular Weights.....	36
Introduction, Part B.....	36
Theory and Review of VPO.....	37
Intermolecular Association.....	39
Infrared Spectroscopy-A Probe for Intermolecular Association.....	44
Other Methods for MW Determination.....	45
Experimental, Part B.....	47
VPO.....	47
Measurements in 1,2-Dichloroethane.....	47
Measurements in Pyridine.....	48
Infrared Spectroscopy.....	48
Nonaqueous Titrations (NAT).....	48
Mass Spectrometry.....	49
Results and Discussion.....	49
Cerro Negro $\overline{MW}$	49
Methodology for Determination of $\overline{MW}$	55
MS Determination of $\overline{MW}$	55
GC Determination of $\overline{MW}$ for Saturates.....	56
Equivalent Weight Methods.....	56
VPO in 1,2-Dichloroethane and Pyridine.....	58
Optimizing Methodology for Determining $\overline{MW}$ for Heavy Oils.....	67
Intermolecular Association.....	68
Summary and Conclusions.....	84
References.....	87

TABLE OF CONTENTS (cont'd)

TABLES AND ILLUSTRATIONS

<u>Table</u>	<u>Page</u>
1 BOM routine petroleum analysis.....	10
2 Physical/chemical properties of Cerro Negro crude and distillates.....	26
3 A comparison of physical/chemical properties of Cerro Negro heavy oil with those of other light, medium, and heavy petroleums, tar sand bitumens, and organic material extracted from oil shale.....	31
4 Comprehensive listing of average equivalent ($\bar{E}W$, g/equivalent) and molecular ($\bar{M}W$, g/mole) weights for Cerro Negro fractions	50
5 Summary of best available $\bar{M}W$ data for Cerro Negro fractions and whole crude.....	52
6 Carboxylic acid molar absorptivities (ϵ_M), dimerization constants (K_D), and the effect of dimerization on apparent $\bar{M}W$ measured by VPO.....	82

Figure

1 Diagram of 4-inch wiped-wall still.....	7
2 Conditions and yields of wiped-wall distillation of Cerro Negro heavy oil.....	8
3 Distillation curves for whole Cerro Negro crude determined by GC (crude oil method) vs actual distillation via the U.S. Bureau of Mines (BOM) procedure.....	13
4 Comparison of distillation profiles for the <200° C wiped-wall distillate obtained by earlier and later versions of the ASTM D 2887 method.....	14
5 GC D 2887 distillation curves for the original <200° C distillate from the wiped-wall still and recut spinning band <200° C and >200° C fractions.....	15
6 Actual GC chromatograms of the standard (Altamont crude, carbon numbers of n-paraffins are designated) and Cerro Negro distillates obtained using dual OV-1 columns.....	18
7 GC boiling point distributions of Cerro Negro wiped-wall distillates...	19
8 GC D 2887 distillation curves for 200-425° C whole distillate vs saturates.....	21
9 GC D 2887 distillation curves for 425-550° C whole distillate vs saturates.....	22
10 GC (lube oil method) distillation curves for 550-700° C whole distillate vs saturates.....	23
11 GC (lube oil method) distillation curves for >700° C whole residue, neutrals, and saturates.....	24
12 Calculated concentration dependence of the reciprocal of apparent molecular weight, i.e., the result which would actually be measured by VPO, for selected values of K_D in the case of a dimerizing substance with a monomeric $\bar{M}W = 400$ (see text).....	43

TABLE OF CONTENTS (cont'd)

TABLES AND ILLUSTRATIONS

<u>Figure</u>	<u>Page</u>
13 Actual concentration dependence of the reciprocal of apparent molecular weight ($\Delta V/C \propto 1/\overline{MW}$) for Cerro Negro 200-425° C fractions in 1,2-dichloroethane.....	61
14 Actual concentration dependence of the reciprocal of apparent molecular weight ($\Delta V/C \propto 1/\overline{MW}$) for Cerro Negro 550-700° C fractions in 1,2-dichloroethane.....	62
15 Actual concentration dependence of the reciprocal of apparent molecular weight ($\Delta V/C \propto 1/\overline{MW}$) for selected Cerro Negro fractions in pyridine.....	63
16 Comparative VPO curves obtained in 1,2-dichloroethane for neutral fractions from three heavy oils.....	64
17 Partial IR spectra of 1,2,3,4-tetrahydrocarbazole in carbon tetrachloride at the indicated concentrations (mg/mL).....	71
18 Partial IR spectra of m-cresol showing frequency and intensity of O-H band as a function of solvent polarity.....	72
19 Partial IR spectra of n-decanoic acid (A) and Cerro Negro 200-425° C acids (B) showing effect of concentration (mg/mL in 1,2-dichloroethane), indicated for each spectrum, on the relative intensity of carbonyl bands corresponding to monomeric (1750 cm^{-1}) and dimeric (1710 cm^{-1}) carboxylic acids.....	73
20 Partial IR spectra of n-decanoic acid showing carbonyl bands as a function of concentration (mg/mL) in carbon tetrachloride (A) and THF (B).....	74
21 Partial IR spectra of p-toluic acid (0.97 mg/mL in 1,2-dichloroethane) with and without the presence of quinoline (molar ratio of p-toluic acid/quinoline = 0.36).....	76
22 Beer's law plots for total IR absorbance of carboxylic acid monomer plus dimer carbonyl bands vs concentration.....	77
23 Plots corresponding to equation 24 for determining equilibrium constants for dimerization of carboxylic acids (see text).....	79
24 Concentration dependence of $1/\overline{MW}$, the reciprocal of the weighted average MW for monomeric and dimeric species, calculated from data in table 6 using equations 13 and 16 (see text).....	83

DO NOT MICROFILM
THIS PAGE

(This page intentionally left blank.)

ABSTRACT

Part A discusses distillation of Cerro Negro heavy oil and general chemical/physical properties determined on each distillate and the residue. Based on GC-simulated distillation results, compounds boiling up to 700° C atmospheric equivalent boiling point (AEBP) were distilled; nevertheless, total distillate yield represented only 55 weight percent of the whole crude. As revealed by comparative data on other crudes contained in the report, overall, chemical/physical properties of Cerro Negro crudes resemble those of tar sand bitumens and other geochemically related organic matter.

Part B examines methodology for determining average molecular weights of Cerro Negro fractions and like materials. The theory and practice of vapor pressure osmometry (VPO) as applied to fossil fuels was critically evaluated through its application to Cerro Negro fractions and pure compounds, and by comparison of VPO results to those from other methods. Both solute-solute and solute-solvent intermolecular associations cause VPO data to be erroneously high, especially in cases where either the solutes and/or solvents are relatively polar. In general, solute-solute associations occur through charge-transfer, London dispersion or similar type of interaction(s) between aromatic moieties, rather than by hydrogen-bonding, or functional group-based interactions. It is highly probable that intermolecular interactions strongly affect other chemical/physical properties such as viscosity and density.

ACKNOWLEDGMENTS

The authors thank the U.S. Department of Energy for financial support. They also thank L. E. Green and coworkers, Hewlett-Packard, Avondale, PA, for their simulated distillation analysis of the 550°-700° C distillate. Finally, appreciation is extended to R. P. Anderson, P. R. Stapp, and W. D. Good of NIPER, and W. D. Peters of U.S. DOE-BPO for reviewing the manuscript and to Ms. Joan Haimson for typing and preparation.

**DO NOT MICROFILM
THIS PAGE**

(This page intentionally left blank.)

DISTILLATION AND DETERMINATION OF "ROUTINE" CHEMICAL/PHYSICAL PROPERTIES

by

J. B. Green, P. L. Grizzle, J. S. Thomson,
J. Y. Shay, B. H. Diehl, K. W. Hornung, and V. Sanchez

PART A. DISTILLATION AND DETERMINATION OF CHEMICAL/PHYSICAL PROPERTIES OTHER THAN MOLECULAR WEIGHT

INTRODUCTION, PART A

Approximately 0.4 barrels of desalted and dewatered Cerro Negro heavy crude was obtained from INTEVEP in mid-1980. An aliquot of the crude was subsequently analyzed by the U.S. Bureau of Mines (BOM) procedure (1) for determining general chemical/physical characteristics of the crude. The results of the BOM analysis, in conjunction with additional inspection properties supplied by INTEVEP, served as a basis for developing strategy and selecting methodology for the ensuing detailed analysis of the crude. This chapter describes the first step in the detailed analysis scheme, distillation, along with general chemical/physical properties determined for the whole crude, its distillates, and the distillation residue.

The primary objective of the large-scale distillation was to improve the quality of and simplify practical aspects of the subsequent separation and analysis steps. For example, the overall sensitivity obtained in mass spectrometric (MS) analysis of a series of distillates is greater than that achievable from analysis of the corresponding whole material because the mass range spanned by each individual distillate is less than that of the whole crude. Also, problems encountered with mass calibration, sample introduction, as well as other practical aspects of MS analysis are minimized by prior distillation of the sample. Similar advantages are obtained in chromatographic separations of distillates over whole crudes, since separation conditions, fraction cut points, etc., can be optimized for each boiling range. In addition, distillation enables determination of chemical/physical properties such as specific gravity, refractive index, and elemental composition as a function of boiling point.

The type of still most consistent with the objective of preparing relatively large volumes of distillates with minimum sample decomposition has been referred to as "short-path," "thin-film," "wiped-wall," or "molecular" distillation apparatus in past work (2-5). In this mode of distillation, the material is mechanically pumped or gravity fed into an evaporator where it is spread into a thin film on a heated glass cylinder by rotating wiper blades. Material sufficiently volatile at the temperature and pressure employed evaporates off the hot surface and condenses on a cold finger positioned a few millimeters from the outer cylindrical wall. The resulting residue and distillate then flow into separate receivers. The main advantages of this approach are: 1) the short time of sample exposure to heat (variable with manufacturer and design, but typically <1 min) and 2) the ability to distill relatively nonvolatile material, up to estimated atmospheric equivalent boiling points (AEBP) of 1400° F (760° C). Its main disadvantage is low distillation efficiency, typically less than one theoretical plate. The boiling ranges of distillates obtained using wiped-wall stills are nearly always determined independently; quite often, gas chromatographic (GC) simulated distillation methods are employed. Because vapor-liquid equilibrium is not even approximately established in this method of distillation, nomographs developed for predicting AEBP in pot-type stills operated under vacuum are inappropriate for determining AEBP from corresponding parameters in wiped-wall distillation. Also, pressure gauges are typically mounted external to the actual evaporator, and thus may not accurately measure effective pressure between the hot evaporative surface and cold finger. Therefore, correlation of distillation conditions versus AEBP of the resulting distillate is empirical and depends on the still's design and construction.

In contrast to methodology described in later chapters dealing with detailed analysis of Cerro Negro and other heavy oils, standardized and/or well-established methods were used here for determining general chemical/physical properties of the crude and distillates, so that the data reported here would be comparable to that obtainable in other laboratories. Also, in most cases, the applicability of a given test procedure to Cerro Negro was not critically examined; hence, the results should be typical of those obtainable by others using the same method, but the method may in fact yield inaccurate results on heavy oils or heavy oil fractions. For example, problems in obtaining complete sample combustion prior to determining elemental nitrogen

in heavy petroleum fractions were recently evaluated (6). Lighter crudes or their fractions are more easily combusted and hence determination of nitrogen, and potentially other elements, is inherently easier and more precise than with heavy crudes, petroleum residues, and like materials. However, because of their importance to the overall characterization of Cerro Negro and their use in calculation of other properties and compositional parameters, average molecular weights of Cerro Negro fractions were determined by several methods, and those results are critically evaluated. Because of its length, the description of the work on average molecular weight measurements appears as a separate section (Part B).

EXPERIMENTAL, PART A

Distillations

GC-Simulated Distillations

Three gas chromatographic (GC) simulated distillation procedures were used to determine boiling point profiles of the whole crude and distillates/residues derived from the crude. Distillates boiling $<550^{\circ}\text{C}$ ($<200^{\circ}$, $200\text{--}425^{\circ}$, and $425\text{--}550^{\circ}\text{C}$) and fractions thereof were analyzed according to ASTM method D 2887 (7). In early work (ca. 1980), dual 6-foot by 1/8-inch OD OV-1 columns were linearly programmed from 0° to 385°C at $12^{\circ}\text{C}/\text{min}$. Use of dual columns and detectors enabled cancellation of baseline drift caused by stationary phase bleed at higher GC oven temperatures. A Perkin-Elmer (Norwalk, CT) Model 900 gas chromatograph was interfaced to a Data General (Southboro, MA) Nova 3 computer with in-house software which performed time-slice integration and other data reduction routines as specified in the ASTM method. The carrier gas (He) flow rate was $30\text{ mL}/\text{min}$ through both columns; the injector and flame ionization detector temperatures were 375°C and 400°C , respectively. The column packing contained 3 (W/W) percent loading of the OV-1 stationary phase on Chromosorb W-H.P. (Manville, Denver, CO) 80-100 mesh solid support and was conditioned at 385°C overnight prior to use. Normal paraffins in a topped sample of Altamont, Utah, crude oil were used to construct the GC retention time/AEBP correlation described in the ASTM method.

In later work (1983 and thereafter), ASTM D 2887 simulated distillations were carried out using a single 1/8-inch OD by 20-inch column packed with 10 (W/W) percent UCW 982 liquid phase coated on Chromosorb G-HP 80/100 mesh solid support (Supelco, Bellefonte, PA). Columns were preconditioned at 100° C and 40 mL/min He flow for 30 min; then the exit end of the column was plugged, and the column was heated under positive He pressure at 350° C for 12 hours. Finally, the column was subjected to 10 temperature program cycles prior to use. The temperature program used for column conditioning and actual analyses was a linear ramp from -30° C to 350° C at 10° C/min with a 2-min hold at 350° C. A Hewlett-Packard (Palo Alto, CA) Model 5880A GC and data system were used for the analysis. Software supplied by the manufacturer performed time-slice integration and other calculations as specified in the ASTM method, as well as correction for baseline drift due to column bleed by subtracting a stored chromatogram from a blank run from each sample chromatogram. Because of the latter capability for baseline subtraction, use of dual columns as in the early method was unnecessary. Other instrumental conditions were as follows: flow rate - 20 mL/min (He), injector temperature - 350° C, and flame ionization detector - 360° C, with hydrogen and air flows optimized for maximum sensitivity. A Hewlett-Packard-supplied reference gas oil (No. 1) was used for quality control of results obtained by this method.

The simulated distillation of the whole Cerro Negro crude was performed under conditions identical to those described above for the later D 2887 analyses, except that a 20-min temperature hold at the maximum GC temperature (350° C) was used instead of the 2-min hold in the D 2887 procedure. In order to determine the percent of the whole crude which did not elute from the GC column, it was necessary to analyze the crude with and without an internal standard mixture of C₁₄-C₁₇ normal paraffins. The area of the internal standard mixture was computed from the chromatogram of the spiked crude, using the chromatogram of the unspiked effectively as a baseline. The resulting area of the internal standard was ratioed with the total area for the crude oil components and multiplied by the weight percent internal standard added to determine the percent of the crude eluted by the GC. Thus, the final boiling point distribution from simulated distillation analysis was corrected for the percent of the crude which did not elute from the GC. This method has been under consideration for adoption by ASTM; further details of the proposed method have been published as ASTM D-2 Proposal P 167 (8). All calculations

and data handling were performed with Hewlett-Packard-supplied software. This method is based on the work of Worman and Green (9) and is required for analyzing any crude containing compounds boiling above 1000° F (538° C). Also, a very similar method was recently published by Petroff, et al. (10).

The 550-700° C heavy distillate and >700° C residue and fractions thereof were analyzed by a third simulated distillation method. This method was similar to that used for the whole crude, but, because these higher boiling fractions did not contain components coeluting with the internal standard, the areas of the internal standard and sample components could be obtained directly from a single analysis of the spiked sample, thereby making analysis of the unspiked sample unnecessary. In this method, an internal standard mixture containing C₁₀-C₁₂ normal paraffins was used. UCW 982 columns used in this procedure were conditioned at 100° C under flowing He as before, but were heated to 380° C for eight hours in the static high temperature conditioning step. The temperature program used in column conditioning and analyses of samples was a linear ramp from 50° C to 380° C at 8° C/min, with a 20-min hold after reaching 380° C. Also, the injector and detector temperatures were slightly higher than in the other methods: 380° C and 400° C, respectively. This method elutes components boiling up to approximately 1150° F (620° C), based on Polywax 655 normal paraffin calibration, which represents the upper limit of any simulated distillation approach using conventional GC instrumentation. All calculations and data reduction were done using software supplied by Hewlett-Packard. Because this method is most commonly applied in industry to analyze lubricating oil base stocks, it is often referred to as the "lube oil" method. Further details of the method are given in Green et al. (11). Petroff, et al. (10) and DiSanzo, et al. (12) reported methods similar to the above, but they used temperature programmed injection and Petroff, et al. (10) employed a precolumn with backflush in their analysis of high boiling fractions.

Small Scale Pot-Type Distillations

Approximately 300 mL of dewatered crude was distilled according to the Bureau of Mines routine method (1). This method provides fractions suitable for analysis via a standardized scheme which are directly comparable to corresponding data for over 9,000 crude oils (13). In addition, the <200° C

distillate from the large-scale wiped-wall distillation, described below, was redistilled on a high efficiency spinning band pot still. The latter was a Perkin-Elmer 91-cm adiabatic still equipped with a Monel band yielding 75 theoretical plates, according to the manufacturer's literature. The spinning band distillation was carried out under nitrogen at atmospheric pressure. The thermocouple measuring overhead vapor temperature was calibrated by distilling propanol ($BP^{760} = 97.2^{\circ} \text{C}$) and tetralin ($BP^{760} = 207^{\circ} \text{C}$). All observed boiling points were corrected to 760 mm Hg (1 atm) pressure.

Large-Scale Wiped-Wall Distillation

A 4-inch Pope Scientific (Menomonee Falls, WI) wiped-wall still was used for distillation of about 15 kg of dewatered Cerro Negro crude. Figure 1 shows details of the apparatus, and figure 2 shows yields of distillates at temperatures and pressures utilized for successive passes through the still. Selection of experimental conditions for a given stage in the distillation was largely based on prior experience with a similar apparatus (2).

Determination of the boiling ranges shown for a given distillate in figure 2 was based on GC-simulated distillation results.

Determination of Physical/Chemical Properties

Some of the carbon, hydrogen, nitrogen, and sulfur (CHNS) and all of the oxygen elemental analyses were done by Huffman Laboratories, Golden, CO. Carbon and hydrogen analyses both at Huffman Laboratories and NIPER were based on combustion in an oxygen atmosphere followed by determination of CO_2 and water. In samples containing >0.5 weight percent nitrogen, N_2 was concurrently determined with carbon dioxide (C) and water (H) to yield elemental nitrogen content. Lower level nitrogen content was measured independently at NIPER using combustion and chemiluminescent measurement of NO (6,14). Sulfur was measured by combustion to SO_2 and subsequent infrared (LECO) (15) or microcoulometric (Dohrman) (16) determination of SO_2 . Controlled pyrolysis followed by measurement of CO was used at Huffman Laboratories for elemental oxygen determinations.

FIGURE 1. - Diagram of 4-inch wiped-wall still

FIGURE 2. - Conditions and yields of wiped-wall distillation of Cerro Negro heavy oil

Elemental V, Ni, and Fe were determined at NIPER by ashing the crude, distillates, and >700° C residue; the ash was subsequently dissolved in mineral acid and the resulting aqueous solution analyzed by flame or flameless atomic absorption spectrophotometry. Thus, 1-gram samples were first charred on a hot plate in Vycor evaporating dishes containing 1 mL of high purity sulfuric acid (Ultrex, J. T. Baker Chemicals, Phillipsburg, NJ). Chars were subsequently ashed in a furnace at 500° C. After cooling, 0.5 mL of nitric and 0.25 mL each of hydrochloric and sulfuric Ultrex high purity acids were added with 2-5 mL high purity water (Milli-Q system, Millipore Corp., Bedford, MA) to each ash, and mild heating was used to dissolve the ashes. After dissolution, each was transferred to a plastic 25-mL volumetric flask and diluted to volume with high purity water. The resulting solutions were analyzed using aqueous standards and blanks containing corresponding concentrations of mineral acids. Ni and V in the crude were also determined at INTEVEP using neutron activation analysis (17).

Determination of average molecular weights is discussed in section 1B. Other chemical and physical tests were performed using standard ASTM (7) and UOP (15) methods. References to specific tests are given in the next section along with the test results.

RESULTS, PART A

Distillations

Table 1 shows results from the standard BOM analysis scheme. Generally, those results show 1) extremely low yields of distillable naphtha and mid-distillates and only moderate yields of gas oil fractions, 2) high relative aromatic content in a given boiling range compared to similar distillates from conventional crudes, and 3) essentially 100-percent naphthene types of saturates in all boiling ranges; i.e., essentially no normal or branched paraffins present. These properties result from the extensive biodegradation and water washing described in modern geochemical models for the Orinoco heavy oil belt (18).

TABLE 1. - BOM routine petroleum analysis

CRUDE PETROLEUM ANALYSIS

BARTLESVILLE ENERGY TECHNOLOGY CENTER
SAMPLE B80013

IDENTIFICATION

CERRO NEGRO FIELD

VENEZUELA
MONAGAS

GENERAL CHARACTERISTICS

GRAVITY, SPECIFIC: 1.013 API: 8.2 POUR POINT, DEG F: 93
 SULFUR, WT PCT: 3.85 NITROGEN, WT PCT: 0.640
 VISCOSITY, SAYBOLT UNIV SEC: COLOR: BROWNISH-BLACK
 AT 100 F > 6000
 AT 130 F > 6000

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1-DISTILLATION AT ATMOSPHERIC PRESSURE 756 MM HG
FIRST DROP AT 282 DEGREES F.

FRAC NO.	CUT TEMP F	VOL PCT	SUM VOL PCT	GRAVITY SPEC (60/60 F)	API	CORR INDEX	REFRACT INDEX, ND (20 C)	SPEC DISP	SU VISC SECS (100 F)	CLOUD POINT F
1	122									
2	167									
3	212									
4	257									
5	302									
6	347									
7	392	1.1	1.1	0.817	41.7	-				
8	437	1.5	2.6	0.850	35.0	48	1.46390	144.6		
9	482	2.8	5.4	0.868	31.5	51	1.47499	148.8		
1/ 10	527	7.0	12.4	0.877	29.8	-				

STAGE 2-DISTILLATION CONTINUED AT 40 MM HG

11	392	0.7	13.1	0.896	26.4	-				
12	437	1.2	14.3	0.916	23.0	61	1.50522	176.7		
13	482	4.5	18.8	0.928	21.0	63	1.51394	183.1	13	< 5
14	527	6.1	24.9	0.942	18.7	67			33	< 5
15	572	8.7	33.6	0.957	16.4	71			94	< 5
RESIDUUM		66.4	100.0	1.063	1.6					

CARBON RESIDUE, WT PCT: OF RES: 27.7 SULFUR, WT PCT OF RES: 4.16
 (CONRADSON) OF CRUDE: 19.3 NITROGEN, WT PCT OF RES: 0.847

APPROXIMATE SUMMARY

	VOL PCT	SP GRAV	API	VISCOSITY
LIGHT GASOLINE	0.0			
TOTAL GASOLINE AND NAPHTHA	1.1	0.817	41.7	
KEROSENE DISTILLATE	0.0			
GAS OIL	22.8	0.895	26.6	
NONVISCIOUS LUBE DISTILLATE	6.1	0.946-0.958	18.0- 16.1	50-100
MEDIUM LUBE DISTILLATE	3.6	0.958-0.966	16.1- 15.0	100-200
VISCIOUS LUBE DISTILLATE	0.0			> 200
RESIDUE	66.4	1.063	1.6	
DISTILLATION LOSS	0.0			

1/ DISTILLATION DISCONTINUED AT 509 DEGREES F.

TABLE 1. - BOM routine petroleum analysis (cont'd)

HYDROCARBON-TYPE ANALYSIS
CRUDE OIL ANALYSIS NO. B80013

FRAC NO.	VOL PCT OF CRUDE	SPEC GRAV	CORR INDEX	AROMATICS VOL PCT OF FRAC	PAR-NAPH VOL PCT OF FRAC	CORR INDEX OF P-N	SPEC GRAV OF P-N
1							
2							
3							
4							
5							
6							
7	1.1	0.817	-	14.9	85.1	31	0.804
8	1.5	0.850	48	19.4	80.6	40	0.835
9	2.8	0.868	51	21.3	78.7	42	0.849
10	7.0	0.877	-	29.7	70.3	37	0.848
11	0.7	0.896	-	34.8	65.2	40	0.864
12	1.2	0.916	61	40.9	59.1	48	0.889

ANALYSIS OF NAPHTHA FRACTIONS				FRAC	NO. OF RINGS PER MOL:		
FR	VOL PCT OF PN	VOL PCT OF FR		NO.	TOTAL	AROM	NAPHTHINES
NO.	NAPH	PAR	NAPH	PAR			
2					12	2.3	0.6
3					14	(INSUFFICIENT DATA)	1.7
4							
5							
6							
7	100.0	0.0	85.1	0.0			

SUMMARY DATA FOR BLENDS

	NAPHTHA BLEND (FR 7-7)	GAS OIL BLEND (FR 8-12)
VOLUME PERCENT OF CRUDE IN BLEND	1.1	13.2
AROMATIC, VOL PCT OF BLEND	14.9	28.0
PARAFFIN-NAPHTHENE, VOL PCT OF BLEND	85.1	72.0
NAPHTHENE, VOL PCT OF BLEND	85.1	
PARAFFIN, VOL PCT OF BLEND	0.0	
NAPHTHENE, VOL PCT OF P-N IN BLEND	100.0	
PARAFFIN, VOL PCT OF P-N IN BLEND	0.0	
NAPHTHENE RING, WT PCT OF P-N IN BLEND	51.9	59.7
PAR + SIDE CHAINS, WT PCT OF P-N IN BLEND	48.1	40.3

Figure 3 shows the boiling point distribution for the whole Cerro Negro crude determined by GC-simulated distillation. The GC method indicated that 42 percent (W/W) of the crude distilled off at 1000° F (538° C), which agrees very well with the gravimetric results (40.8 weight percent at 550° C) from the wiped-wall distillation shown in figure 2. BOM distillation results, shown in addition to the GC data in figure 3, track the GC results reasonably well; however, distillation curves obtained from actual distillations are subject to deviations caused by nonideal behavior such as azeotropic effects, errors in AEBP predicted from nomographs based on the Clausius-Clapeyron or similar relations, distillation column efficiency, and a greater possibility of human error. Butler (19) reviewed the correlation between results from ASTM GC-simulated distillations versus actual D 86 distillations and found discrepancies of similar magnitude to those in figure 3.

Figure 4 compares GC distillation curves for the <200° C distillate from the wiped-wall distillation obtained with the earlier dual OV-1 column and later single UCW 982 column versions of the ASTM D 2887 GC method. Considering that entirely different columns, GCs, data systems, and operators were utilized, and that the sample itself had aged for seven years between the two analyses, excellent agreement was obtained.

Both data sets in figure 4 indicated that a substantial proportion of the distillate from the wiped-wall still boiled in excess of 200° C. For this reason, the wiped-wall distillate was redistilled using a pot-type spinning band still, as described in the Experimental section. Thus, 39.4 weight percent of the original "<200° C" distillate was recovered in the <200° C fraction from the spinning band distillation. Figure 5 shows GC distillation curves for the original wiped-wall distillate and the recut spinning band distillate and residue. The dashed vertical line on the figure, intersecting the curve for the wiped-wall distillate at 39.4 weight percent and 210° C, indicates the very slight degree of overlap between the recut spinning band fractions. Correction of the observed temperature and pressure at the cut point of the spinning band distillation resulted in a calculated AEBP of 194° C, which is significantly lower than the corresponding GC result (210° C). This discrepancy probably resulted in part from formation of

FIGURE 3. - Distillation curves for whole Cerro Negro crude determined by GC (crude oil method) vs actual distillation via the U.S. Bureau of Mines (BOM) procedure.

FIGURE 4. - Comparison of distillation profiles for the <200° C wiped-wall distillate obtained by earlier and later versions of the ASTM D 2887 method.

FIGURE 5. - GC D 2887 distillation curves for the original <200° C distillate from the wiped-wall still and recut spinning band <200° C and >200° C fractions. The dashed line defines the cutpoint (210° C) between the two spinning fractions.

minimum boiling azeotropes between the predominant cycloparaffinic and aromatic species present. For example, benzene (BP 80.1) and cyclohexane (BP 81.4) azeotrope at 77.8° C (20). Also, the D 2887 *n*-paraffin-based calibration method for converting GC retention time to AEBP generally should overestimate AEBP for naphthenic-aromatic crudes such as Cerro Negro (21).

Reasonable agreement was obtained between the BOM distillation in which 1.1 volume percent (0.9 weight percent) of <200° C distillate was obtained and the spinning band redistillation, which yielded 1.02 weight percent* of the whole crude as <200° C distillate. A significantly higher yield of <425° C distillate was obtained with the BOM as compared to the wiped-wall distillation, however. In the case of the BOM distillation, 33.6 volume percent (30.3 weight percent) was obtained at 572° F and 40 mm Hg pressure (AEBP = 421° C, see table 1), whereas the wiped-wall still yielded a cumulative total of only 25.0 weight percent of distillate at a GC-determined final AEBP of 425° C. The reasons for this discrepancy are largely the same as those advanced earlier for the difference between the apparent cut point for the spinning band distillation calculated from temperature and pressure observed during the actual distillation (194° C) and that from the simulated distillation analysis of the products (210° C). That is, the GC-determined endpoint for the 200-425° C wiped-wall distillate is significantly higher than that which would have been calculated from actual distillation parameters. In fact, based on the BOM distillation data plotted in figure 3, 25 weight percent distillate from the crude should have been obtainable at a measured AEBP of 402° C. Arguments as to which means for assessing distillation temperature is most "correct" are largely futile because each is subject to several sources of error. However, it is important to recognize that the GC-determined cut point temperatures for higher boiling distillates from the wiped-wall distillation, for which no corresponding pot-still data are available, are in all probability higher than those which would be obtained from a pot-type distillation.

*Wiped-wall <200° C distillate yield = 2.59 wt % (fig. 2); spinning band redistillation resulted in 39.4% of the original wiped-wall distillate as <200° C product.

Because wiped-wall distillate cut points must be independently assessed, the GC-based temperature scale is used throughout this and later chapters to describe boiling points, since a uniform method for measuring boiling point is necessary for self-consistency. For example, the good agreement mentioned earlier for the yield of $<1000^{\circ}\text{F}$ material predicted from the GC analysis of the whole crude and gravimetric yields from the wiped-wall distillation would not have been possible had some method other than GC had been used to determine boiling ranges of the wiped-wall distillates.

Figure 6 shows actual GC traces (dual OV-1 column method) from simulated distillation analysis of the $<200^{\circ}$, $200-425^{\circ}$, $425-550^{\circ}$, and $550-700^{\circ}\text{C}$ wiped-wall distillates. The chromatogram of the standard (topped Altamont crude) is also shown in the figure. The figure shows 1) appreciable overlap between neighboring distillates, 2) lack of any discernable *n*-paraffin peaks in any of the distillates (cf. the standard), and 3) incomplete elution of the $550-700^{\circ}\text{C}$ distillate from the GC. All of the above observations were expected in light of the 1) known poor efficiency of wiped-wall stills, 2) preference of microorganisms for *n*-paraffins, and 3) approximate 580°C limit of the dual OV-1 GC method.

Figure 7 shows the distillate boiling point distributions calculated from the GC-simulated distillations. Analysis of the $>700^{\circ}\text{C}$ residue showed a negligible amount of material distillable at temperatures $\leq 1150^{\circ}\text{F}$ (620°C). The distillation cut points were determined from plots similar to those in the figure, except that the "percent off" axis was weighted by the yield of each distillate to express results on a whole crude rather than whole distillate basis. For example, the $<200^{\circ}\text{C}$ distillate represented only 2.59 weight percent of the crude and the $200-425^{\circ}\text{C}$ distillate comprised 22.42 weight percent (see figure 2); the apparent carry-over of the $<200^{\circ}\text{C}$ distillate into the range of $200-425^{\circ}\text{C}$ distillate is greatly exaggerated when their boiling point distributions are plotted on normalized 0-100 percent scales such as in figure 7. The cut point of a given stage in the distillation was defined as the temperature where the relative overlap of consecutive distillates was equal. Determination of the cut point in this manner was illustrated earlier in figure 5; in that case, the dashed vertical line indicated approximately 5 percent overlap for each of the two spinning band fractions at 210°C .

FIGURE 6. Actual GC chromatograms of the standard (Altamont crude, carbon numbers of *n*-paraffins are designated) and Cerro Negro distillates obtained using dual OV-1 columns. The 550-700° C distillate was rechromatographed (lube oil method) for determination of its boiling point distribution.

CUMULATIVE PERCENT OFF

FIGURE 7. - GC boiling point distributions of Cerro Negro wiped-wall distillates.

In the case of the wiped-wall distillates, the extent of overlap typically ranged from 10 to 20 percent; hence, the cut points reported were rounded to the nearest 25° C to avoid implication of a highly efficient distillation. In the case of the 550-700° C distillate, where the "lube oil" GC analysis yielded only a partial distillation curve, an extrapolation of the available data to 100 percent off was performed--assuming that the distillation curve exhibited a sigmoidal shape analogous to those of the lower boiling distillates. Also, the degree of overlap between the 550-700° C distillate and >700° C residue was assumed to be comparable to that of the lower boiling fractions. In any case, the cited 700° C cut point obviously carries the greatest uncertainty because of those assumptions.

For reasons discussed in the second part of this chapter, the boiling point distributions of saturated hydrocarbon fractions isolated using liquid chromatographic methods (Chapter 2) were also determined. Those results are shown in figures 8-11, along with the curve of the corresponding whole distillate/residue for comparison. Especially in the cases of saturates from the 550-700° C distillate and >700° C residue, the saturates exhibited significantly greater volatility than the bulk of the distillate/residue. The whole neutral fraction from the >700° C residue, which contains the saturate and neutral-aromatic types (Chapter 2), was also analyzed by simulated distillation and found to exhibit a volatility similar to that of the whole residue (figure 11). Although somewhat speculative, the best present explanation for the abnormally high volatility of saturates in the 550-700° C distillate and >700° C residue is the existence of some type of chemical interaction of saturates with the other components which causes them to distill at higher effective AEBPs. Boduszynski (5) reported a similar phenomenon. He separated "nondistillable" residues from wiped-wall distillations according to solubility, i.e., pentane solubles, cyclohexane solubles, toluene solubles, and methylene chloride/methanol solubles, and found that the pentane soluble fraction, which probably contained the bulk of the saturated hydrocarbons, exhibited appreciable volatility after its separation. Thus, this work and that of Boduszynski support the concept of intermolecular interactions affecting distillation behavior, especially of higher boiling components, during wiped-wall distillation. These effects may be analogous to azeotropes and other nonideal behavior known to occur in pot-type distillations.

FIGURE 8. - GC D 2887 distillation curves for 200-425° C whole distillate vs saturates.

FIGURE 9. - GC D 2887 distillation curves for 425-550° C whole distillate vs saturates.

FIGURE 10. - GC (lube oil method) distillation curves for 550-700° C whole distillate vs saturates.

FIGURE 11. - GC (lube oil method) distillation curves for >700° C whole residue, neutrals, and saturates.

Alternately, the apparent differences between volatility of saturates versus whole distillates could be an artifact of the GC method itself. For example, polycyclic aromatic and/or polar compounds could interact with the GC liquid phase and/or solid support and elute at temperatures higher than those corresponding to their respective boiling points. Obviously, simulated distillation methods are designed to minimize this potential source of error, yet the trend in increased apparent volatility of saturates versus the whole distillate with increasing boiling range is consistent with the above effect. However, if one chooses this explanation as the correct one, he is forced to conclude that the $>700^{\circ}\text{C}$ residue would analyze as 67 percent distillable at 620°C using the ideal GC system where adsorption effects were absent! In one aspect, the arguments advanced in this and the preceding paragraph are quite similar; i.e., the apparent volatility of "high boiling" compounds is suppressed by interactions either among the components themselves and/or with GC column packings. This pronounced tendency for self-association and, presumably, adsorption onto solids also greatly affects their apparent molecular weight, as discussed in section B of this chapter.

Physical/Chemical Properties

Table 2 summarizes chemical/physical properties determined on the whole crude and the wiped-wall distillates/residue. Elemental CHNOS and Ni, V, and Fe balances over the distillates agreed very well with those of the whole crude, as shown in table 2. Some loss of oxygen occurred due to a small amount of water in the "as received" crude. Agreement between atomic absorption and neutron activation results for Ni and V in the whole crude was excellent. Specific gravity of the whole crude was slightly higher than that calculated from the distillates; this difference resulted from small losses of residues from still hold-up (only 98.78 percent of charged material was recovered). Balances for most other properties were not obtained because the methods employed were only applicable to certain boiling ranges. In general, results in table 2 showed the expected increases in aromaticity and heteroatom content with increasing boiling point. Elemental sodium content of the as received crude was 129 ± 3 ppm, which corresponds to a salt content (NaCl) of 110 lb/1000 bbl.

TABLE 2. - Physical/chemical properties of Cerro Negro crude and distillates

	Boiling Range, ° C						Crude Balance ¹
	Crude	<200	200-425	425-550	550-700	>700	
Distillate Yield, wt %	--	2.59	22.42	15.80	12.61	45.36	98.78
Elemental analysis							
C, wt %	84.28	85.96	84.86	84.58	84.35	83.65	84.23
H, wt %	10.42	12.88	11.61	10.92	10.77	9.28	10.36
H/C, atomic ratio	1.473	1.785	1.631	1.538	1.521	1.322	1.466
N, wt %	0.64	0.002	0.091	0.34	0.50	1.16	0.66
O, wt %	0.86	0.39	0.13	0.45	0.55	0.89	0.58
S, wt %	3.81	1.02	2.90	3.46	4.01	4.56	3.80
Ni, ppm (wt)	105 (101) ²	0	0	0	24.8	228	107
V, ppm (wt)	454 (445) ²	0	0	0	107	994	464
Fe, ppm (wt)	93	0	0	0	2.1	203	92
Specific gravity, 60° F (D 4052) ³	1.013	0.857	0.937	0.987	0.997	1.052	1.003
API gravity, 60° F ⁴	8.2	33.6	19.5	11.9	10.4	3.0	9.6
Refractive index, n _D ²⁰ (D 1218)	--	1.46735	1.51412	1.54688	--	--	--
Aniline point, °F (D 611)	--	--	110.2	120.3	--	--	--
Cetane index (D 976)	--	--	32.51	8.18	--	--	--
Freezing point, °F (D 2386)	--	--	5.0	--	--	--	--
Cloud point, °F (D 2500)	--	--	<-10	--	--	--	--
Pour point, °F (D 97)	100	<-5	<-5	45	95	--	--
Conradson carbon (D 524)							
Residue, wt % ⁵	--	--	--	--	9.33	29.29	14.46
Asphaltenes, wt % (D 3279)	13.26	--	--	--	--	33.19	15.05
Average molecular weight (see part B) g/mole	--	175	267	386	481	996	638
Acid neutralization No. (D 664) mg KOH/g	2.67	0.68	4.79	7.03	6.40	1.90	3.87
Base neutralization No. (D 664)	0.71	ND ⁶	ND	ND	ND	1.25	0.57
Mercaptans, ppm (UOP 163)	--	22.3	54.7	--	--	--	--
H ₂ S, ppm (UOP 163)	--	<1	<1	--	--	--	<1

¹ Crude balance was calculated from results on individual distillates and distillate yields.

² Ni and V data in parentheses are neutron activation results determined at INTEVEP.

³ Test numbers preceded by "D" are ASTM methods.

⁴ API gravity = [141.5/specific gravity (60° F)] - 131.5.

⁵ Modified D524 was used to obtain Ramsbottom carbon residues, which were then used to calculate Conradson carbon residues.

⁶ ND = none detected.

TABLE 2. - Physical/chemical properties of Cerro Negro crude and distillates (cont.)

Distillate Yield, wt %	Crude	Boiling Range, ° C					Crude Balance ¹
		<200	200-425	425-550	550-700	>700	
	--	2.59	22.42	15.80	12.61	45.36	98.78
Viscosity, cSt (SUS) D 445							
77° F		2.45 (34.0) ²					
100° F		1.94 (32.4)	19.83 (97.1)				
130° F			9.98 (58.9)	543.4 (2522)			
180° F	1191 (5,545)			78.76 (366.8)	970 (4515)	--	--
210° F	422.4 (1,970)					--	--
250° F					82.71 (386.5)	--	--

¹ Crude balance was calculated from results on individual distillates and distillate yields.

² Viscosities in parentheses are SUS.

DISCUSSION, PART A

Distillation

Historically, the refining industry has relied heavily on distillation technology. Thus, the majority of schemes for characterizing crudes, e.g., the BOM procedure used here, is based on defining composition and properties as a function of boiling point. For fractions boiling below 1000° F (538° C), this approach works well because AEBP can be defined by any of several methods. Of course, the different methods for distilling and/or obtaining distillation distributions do not give exactly the same results, but correlations are available for using results from one method to predict those from another; e.g., (19,22). However, the AEBP approach largely breaks down for material boiling above 1000° F (538° C) for reasons including the following:

1. Distillation of >1000° F material requires the use of wiped-wall or similar apparatus; temperature and pressure readings taken during use of this type of apparatus cannot be used directly to calculate AEBP.
2. Even AEBPs of pure compounds, such as n-paraffins, boiling above 1000° F are determined by extrapolation of data for lower boiling compounds; e.g. see (21). Thus, no directly measured AEBP data exist for materials boiling >1000° F.
3. Conventional GC-simulated distillation methods extend only to ca. 620° C (1150° F).
4. The accuracy of the n-paraffin-based GC retention time - AEBP calibration for high boiling compounds, which typically are predominantly aromatic, is largely unknown.

The limitations cited in the preceding paragraph are widely recognized, and some recently reported work makes significant progress toward overcoming them. For example, GC-simulated distillation has been extended to AEBPs up to 800° C (1475° F) using special high-temperature GCs and columns (23,24). Supercritical fluid chromatographic (25,26) and vacuum thermogravimetric methods (27,28) have also been used to obtain boiling point distributions for high-boiling fractions. These methods all rely on n-paraffin AEBP calibration; Glinzer recently reported an improved formula for calculating AEBP of high-boiling n-paraffins (21). Recently manufactured wiped-wall

distillation apparatus exhibits improved reproducibility and ease of operation but is limited to essentially the same temperature range as the apparatus used here (ca. $\leq 760^{\circ}\text{C}$). Thus, the newer simulated distillation methods are adequate to determine "AEBP" of the even highest boiling wiped-wall distillates. At present, there appears to be no feasible means for extending the range of wiped-wall distillations without entering temperature ranges where significant sample decomposition would probably occur.

Alternate approaches for characterizing heavy petroleums include defining "boiling range" simply in terms of carbon numbers of n-paraffins rather than AEBP. This approach circumvents controversies concerning accuracy of extrapolated AEBP data for n-paraffins and correlation of AEBP of aromatic compounds with those of n-paraffins. Also, since current methods for defining "AEBP" of high-boiling fractions use n-paraffin calibration, a "temperature scale" expressed in terms of paraffinic carbon number would require less data manipulation and remove the false implication that the GC-, supercritical-fluid-chromatographic-, or vacuum-thermogravimetric-derived boiling points would match those obtained from actual conventional distillations.

Given the upper temperature limit of even wiped-wall distillation, alternate methods should be explored for further fractionation of residues according to "AEBP" or molecular weight. Methods based on solubility, such as the one mentioned earlier by Boduszynski (5), may approximately separate on a molecular size or volatility basis. Unpublished work at NIPER indicates that supercritical extraction may also yield fractions of increasing "AEBP" as the severity of the extraction increases. For very heavy petroleums, such as Cerro Negro, where the distillation residue was nearly 50 percent of the whole crude, further separation of the residue would greatly improve the characterization of the crude. Any mode of separation which would yield subfractions of the distillation residue eluting at progressively higher n-paraffin carbon numbers in a simulated distillation-type analysis would be consistent with distillation methods used to separate the distillable materials. As mentioned earlier, simulated distillation methods should be used throughout for consistent evaluation of relative boiling range of the distillates as well as residue fractions.

Chemical/Physical Properties of Heavy Crudes

For comparison with Cerro Negro, a more limited set of chemical/physical properties of other crudes was taken from the literature (2,3,29-34) and is summarized in table 3. The crudes are arranged in order of decreasing API gravity from left (highest) to right (lowest). In many cases, complete sets of data for table 3 were not available. Thus, where possible, appropriate properties were estimated from available data from a given crude or a closely related one and shown in parentheses. Also, cited distillation profiles frequently used slightly different cut points than those in the table. In those cases, linear interpolation was used to calculate the percent distilled at the cut points given in table 3. Interpolated distillation results are not shown in parentheses since they represent only slight adjustments of reported results. Distillation results shown in parentheses were either estimated from molecular weight profiles (e.g., Arabian Light) or from the distillation profile of another sample taken from the same field (e.g., Boscan). Estimated molecular weights were derived from distillation data and n-alkane boiling point/molecular weight correlations (21). Estimates for elemental composition were derived from those of similar crudes. Viscosity at 77° F was determined by conversion of results given at other temperatures using correlations given in ASTM D 2161.

As evidenced by the high sulfur content of both the crude and distillates, high asphaltene and carbon residue yields, high metal and acid neutralization numbers, and overall low yield of distillate, Cerro Negro is an extremely low-quality refinery feedstock. As table 3 shows, Cerro Negro properties do not compare favorably to other heavy petroleums such as Maya, which is known to cause problems in present-day refineries, or even to tar sand bitumens. Only Boscan, a western Venezuelan heavy oil, has as negative a refining outlook as Cerro Negro. Boscan is higher in metals than Cerro Negro and contains a slightly higher percentage of >550° C material. Other properties indicate a higher aromaticity for Cerro Negro, however.

As Boduszynski (5,35) has previously pointed out, many of the properties which are often assumed to follow API gravity--such as molecular weight, average boiling point, and viscosity--in fact correlate poorly with API or specific gravity over a wide range of crudes such as in table 3.

TABLE 3. - A comparison of physical/chemical properties of Cerro Negro heavy oil with those of other light, medium, and heavy petroleums, tar sand bitumens, and organic material extracted from oil shale¹

Fuel Type	Light Petroleum	Medium Petroleum	Heavy Petroleum	Bitumen	Heavy Petroleum	Bitumen	Bitumen	Bitumen	Heavy Petroleum	Heavy Petroleum	Oil Shale
Source Designation	Arabian Light	Prudhoe Bay	Maya	NW Asphalt Ridge	Wilmington	Athabasca	Tar Sand Triangle	P.R. Spring	Boscan	Cerro Negro	Green River
State (USA)/Country	Saudia Arabia	Alaska/USA	Mexico	Utah/USA	CA/USA	Canada	Utah/USA	Utah/USA	Venezuela	Venezuela	CO/USA ⁶
References	3	2	27	28	27	28	28	28	29,30,31	This work	32
Property											
Elemental composition, wt %											
C	(85.0) ²	(86.0)	83.86	85.28	82.33	82.57	84.04	84.44	82.5	84.28	80.4
H	(11.9)	(11.7)	11.52	11.72	10.75	10.28	10.14	11.05	10.4	10.42	10.5
N	0.098	0.23	0.49	1.02	1.19	0.47	0.46	1.00	0.6	0.64	2.6
O ⁴	-- ³	(1.0)	3.77	1.14	1.55	1.78	1.13	2.20	0.76	0.86	4.7
S	1.81	0.82	3.34	0.59	1.93	4.86	4.38	0.75	5.5	3.81	0.5
H/C, atomic ratio	(1.66)	(1.62)	1.638	1.638	1.556	1.484	1.438	1.560	1.50	1.474	1.56
Metal content, ppm (w/w)											
Ni	3.2	(15)	49	120	72	112	53	98	122	105	--
V	15.5	(30)	251	25	53	180	108	25	1318	454	--
Fe	1.1	--	4	--	51	--	--	--	--	93	--
Specific gravity (60° F)	0.856	0.893	0.948	0.970	0.971	0.989	0.992	0.998	0.998	1.013	--
API gravity	33.8	27.0	17.8	14.4	14.2	11.6	11.1	10.3	10.3	8.2	--
Pour point (°F)	5	15	5	--	25	--	--	--	60	80	68
Kinematic Viscosity (poise at 77° F)	0.05	0.21	6.01	29500	24.0	6380	12990	325000	899	3853	--
Carbon residue (wt %)	3.58	4.7	14.24	3.5	10.82	16.11	21.6	12.5	(5.5)	19.3	--
Asphaltenes (wt %)	(<3)	(4.5)	11.7	6.3	3.7	16.4	26.0	16.0	(>14)	13.3	(5)
Average molecular weight (VPO)	(270)	(250)	(420)	668	(460)	568	578	820	(>700)	638	452

¹ Materials are listed in order of decreasing API gravity (if known).

² Data in parentheses are estimates based on results from similar crudes or other properties for which data were available.

³ A dash indicates that result was unavailable and could not be reasonably estimated.

⁴ Oxygen content includes that from water in crude.

⁵ Interpolation of distillation results, e.g., adjustment of actual percent distilled at 308° C to corresponding amount at 300° C, was usually necessary.

⁶ Material extracted at 400° C, 4525 psi, with supercritical (1:1) water-methanol. Yield = 89.5 wt % of total organic matter in shale.

TABLE 3. - A comparison of physical/chemical properties of Cerro Negro heavy oil with those of other light, medium, and heavy petroleum, tar sand bitumens, and organic material extracted from oil shale¹ (cont.)

Fuel Type	Light Petroleum	Medium Petroleum	Heavy Petroleum	Bitumen	Heavy Petroleum	Bitumen	Bitumen	Bitumen	Heavy Petroleum	Heavy Petroleum	Oil Shale Extract
Source Designation	Arabian Light	Prudhoe Bay	Maya	NW Asphalt Ridge	Wilmington	Athabasca	Tar Sand Triangle	P.R. Spring	Boscan	Cerro Negro	Green River
State (USA)/Country	Saudia Arabia	Alaska/USA	Mexico	Utah/USA	CA/USA	Canada	Utah/USA	Utah/USA	Venezuela	Venezuela	CO/USA ⁶
References	3	2	27	28	27	28	28	28	29,30,31	This work	32

Distillation Profiles ⁵											
Cumulative wt % distilled at											
	°C	°F									
100	212	(6) ²	3.8	0	-- ³	0	--	--	--	(--)	0
150	302	(20)	10.0	3.5	--	2	--	--	--	(--)	0.2
200	392	(28)	16.9	9	2.3	5	3.0	1.7	0.7	(3.4)	0.8
250	482	(40)	26.0	16	4.4	12	6.5	4.8	2.4	(7.3)	3.1
300	572	(45)	31.1	24	7.5	20	11.8	10.1	5.3	(11.9)	7.0
350	662	(55)	43.8	32	11.0	28	18.3	16.5	8.8	(14.0)	13.5
400	752	61	53.5	40	15.8	37	25.3	23.3	13.0	(23.8)	21.6
450	842	(68)	60.0	49	24.6	46	32.7	30.3	19.2	(--)	27.8
500	932	75	66.6	56	35.4	55	39.6	36.2	24.5	(--)	38.2
550	1022	81	72.5	63	46.0	62	46.1	41.1	29.0	(38)	42.9
>550	>1022	19	27.5	37	54.0	38	53.9	58.9	71.0	(52)	57.1

¹ Materials are listed in order of decreasing API gravity (if known).

² Data in parentheses are estimates based on results from similar crudes or other properties for which data were available.

³ A dash indicates that result was unavailable and could not be reasonably estimated.

⁴ Oxygen content includes that from water in crude.

⁵ Interpolation of distillation results, e.g., adjustment of actual percent distilled at 308° C to corresponding amount at 300° C, was usually necessary.

⁶ Material extracted at 400° C, 4525 psi, with supercritical (1:1) water methanol. Yield = 89.5 wt % of total organic matter in shale.

The property which is most difficult to correlate is viscosity. For example, data in table 3 are clearly insufficient for explaining the consistently greater viscosities of tar sand bitumens over the other heavy petroleums. Even when comparing Boscan versus Cerro Negro heavy petroleums, there are no conclusive data which adequately explain the fourfold higher viscosity of Cerro Negro. However, in related work performed at NIPER, it was found that addition of 5 percent toluene decreased the viscosity of one heavy petroleum by more than one-half. Thus, the lesser viscosity of Boscan may relate to its greater light distillate content, for example. Related work on viscosities of coal liquids has indicated a significant impact of acid-base pairing toward increasing viscosity (36). Molecular weight and aromaticity also have significant effects on viscosity. Overall, viscosity is probably the property which is most sensitive to detailed fuel composition.

The H/C atomic ratio, carbon residue, and specific or API gravity all indicate relative aromatic content. Carbon residue in particular reflects content of highly condensed aromatics with high coke-forming tendencies. Cerro Negro has the second highest carbon residue of the crudes listed; Tar Sand Triangle bitumen has the highest. Athabasca bitumen and Maya heavy petroleum have the third and fourth highest carbon residues, respectively. Neither H/C ratios nor specific gravities correlate consistently with carbon residues or each other. However, taken together, the three sets of data indicate: 1) an abnormally high concentration of carbon-forming species in Maya relative to its relatively saturated bulk hydrocarbon matrix, 2) a relatively high abundance of noncoke-forming aromatics and cycloalkylaromatics in Cerro Negro which contribute to its high overall specific gravity, and 3) higher concentrations of low density species such as paraffins in tar sand bitumens.

A few generalizations can be made concerning concentrations of metals and heteroatoms in the various fuels. For example, based on its nitrogen and oxygen content, the oil shale extract contains a much higher proportion of acidic and basic compounds than the other fuels. Furthermore, separation results revealed that only 27 percent of that material was neutral in character (37). The metals content of heavy petroleum generally exceeds that of tar sand bitumens of comparable API gravity. The sulfur content of bitumens is quite variable; sulfur in heavy petroleum usually exceeds 3 percent by weight.

Asphaltene content and average molecular weight are currently too experimentally variable and ill defined to be useful for ranking fuels or correlating other properties.

As discussed earlier, distillation profiles for bitumens and heavy petroleums are of limited value because they currently are limited to 550° C using conventional GC methods. For example, only 29 percent of the P.R. Spring bitumen was distillable at 550° C (1022° F). As discussed earlier, improved methods for obtaining boiling point profiles of >550° C residues are in various stages of development. As these become more available, more meaningful comparisons of the distillation profiles of bitumens versus heavy petroleums, for example, should be possible.

The similarity of the Cerro Negro oil to tar sand bitumens is expected, since tar sand bitumens are also heavy, highly biodegraded oils. For example, although they are generally referred to as tar sands, the Athabasca deposits were formed by the migration of conventional petroleum into sand reservoirs followed by bacterial degradation of the oils with the passage of fresh water through the reservoirs. Formation of Cerro Negro was generally similar (18). In general, Cerro Negro is less viscous than bitumens but higher in metal content. Boscan, a western Venezuela heavy oil, has higher sulfur and metal contents than Cerro Negro but lower specific gravity, viscosity, and much lower carbon residue. Properties such as metal content depend on the organic source and thermal maturity of a given oil. The drastic differences in chemical/physical properties of conventional versus heavy petroleum or bitumen observed may be similarly rationalized from geochemical correlations.

SUMMARY AND CONCLUSIONS, PART A

Cerro Negro heavy petroleum was successfully distilled into <200°, 200-425°, 425-550°, and 550-700° C distillates and >700° C residue. Chemical/physical properties on these materials indicated substantial overlap between neighboring distillates but little or no decomposition resulting from the distillation process. Both of these findings agree with prior experience in wiped-wall distillation. The resulting distillates and residue are suitable for further analysis to determine the detailed composition of Cerro Negro heavy petroleum.

By itself, distillation is inadequate for fractionating heavy crudes by boiling point because of their substantial proportions of undistillable residues. Simulated distillation-type methods are best suited for measuring boiling ranges of heavy oil fractions because they can be independently applied to fractions produced by distillation or other methods, and they can be applied to fractions that exhibit volatility corresponding to n-paraffins as high as C₁₀₀. Intermolecular interactions may influence the apparent volatility of saturated hydrocarbons, and potentially other compound types, during wiped-wall distillation.

Chemical/physical properties of Cerro Negro crude resemble those of tar sand bitumens and other geochemically related organic matter. It exhibits a lower API gravity and over-all volatility, and higher heteroatom and metal contents, as well as more pronounced aromaticity than most other heavy petroleums such as those from California, Alaska, and Mexico.

PART B. DETERMINATION OF AVERAGE MOLECULAR WEIGHTS

INTRODUCTION, PART B

Unlike the atmospheric equivalent boiling points (AEBP) discussed in section A, molecular weight (MW) distributions or averages have explicit meaning throughout the entire range of crude components. That is, MW's do not depend on extrapolation or correlations, and at least in theory do not depend on the method used by their determination, except that some methods yield weight average MW while others yield number average MW ($\overline{MW}$), for example. Thus, problems with obtaining reliable $\overline{MW}$, especially for higher MW fractions, stem entirely from difficulties encountered in their experimental determination.

In general, MW increases with AEBP and vice versa. However, because of effects of chemical structure on AEBP as well as non-ideal behavior frequently encountered in distillations, the correlation is imprecise. For example, Boduszynski (5,35) has examined the relationship of MW with AEBP for several crudes and found that although $\overline{MW}$ generally increased with AEBP, the MW distributions showed much more overlap than AEBP and that the MW distributions themselves broadened significantly with increasing AEBP. From a resid processing standpoint, both parameters are significant; yet, in theory MW distributions should give the most accurate measure of the degree of cracking required to achieve significant conversion to distillable material.

A variety of methods have been applied to $\overline{MW}$ determinations; e.g., size exclusion liquid chromatography (SEC) (38-44), mass spectrometry (MS) (5,44-49), a diffusion based method (50,51), vapor pressure osmometry (VPO) (45,52-57), and most recently NMR (58). The standard ASTM VPO method (D 2503) is perhaps the most commonly used method for estimation of $\overline{MW}$. In addition, the VPO method is frequently used to calibrate other methods, especially SEC (38,40,59). MS methods have the greatest potential for quantitative determination of MW distributions, but problems with incomplete volatilization and inadequate knowledge of variations of MS sensitivity with compound type, MW, and ionization mode prevent their rigorous application to petroleum fractions exhibiting high MW/low volatility.

Since, as explained in part A of this chapter, standard methods were used as much as possible for determination of routine chemical/physical properties,

initial $\overline{MW}$ data for the crude and distillates were determined using the standard VPO method, ASTM D 2503. However, unlike other properties determined, no quantitative correlation of the $\overline{MW}$ results was obtainable for individual distillates/residue and that for the whole crude. Given the excellent balances for other properties over the distillation, e.g., elemental composition, the most probable explanation for the disparity in $\overline{MW}$ data was that the method yielded erroneous results for the crude and/or one or more of the distillates/residue. Thus, the pursuit of this problem ultimately led to the work described in this section. The original scope of work, i.e., determining the problem with the Cerro Negro $\overline{MW}$ data, gradually mushroomed to a critical evaluation of the VPO method itself and examination of the general problem of determining $\overline{MW}$ of heavy crudes. The objectives of the work similarly broadened during its course to include the following: 1) to determine the limitations and overall applicability of the VPO method, 2) to determine $\overline{MW}$ of Cerro Negro distillates/residue and compound types within each distillate/residue, and 3) to determine best available methods for estimating $\overline{MW}$ for heavy crudes and their fractions.

Theory and Review of VPO

The major thrust of VPO theory and applications has been in polymer analysis (60). The classic relation between osmotic pressure (Π) and MW (in cases of mixtures, number average MW) is that developed by Van't Hoff:

$$\left(\frac{\Pi}{C}\right)_0 = \frac{RT}{\overline{MW}} \quad (1)$$

C = concentration, (w/v)

R = ideal gas constant

T = °K

$(\Pi/C)_0 = \Pi/C$ at infinite dilution.

For polymers, the following series describes the relation between Π/C and $(\Pi/C)_0$:

$$\pi/C = (\pi/C)_0 [1 + A_2MWC + A_3MWC^2 + \dots], \quad (2)$$

where A_2 , A_3 , etc., are virial coefficients.

For low values of C , C^2 and higher terms in the expansion typically can be neglected, thus:

$$\pi/C \approx (\pi/C)_0 [1 + A_2MWC]. \quad (3)$$

Therefore, $(\pi/C)_0$ is determined by linear extrapolation of plots of π/C versus C to zero C (slope = $A_2 MW$). The resulting $(\pi/C)_0$ is then used to calculate MW using equation (1).

Prior applications of VPO for determining $\overline{MW}$ of fossil fuels or their fractions have typically used the above approach. Optimization of experimental variables, such as the type of solvent, temperature employed for measurements of π , and chemical modification of the sample prior to MW measurement has received the greatest attention (45,52, 54-57). Since most of the potential sources of error in VPO measurements lead to erroneously high rather than low results, the experimental procedure is typically adjusted to obtain the lowest $\overline{MW}$ possible for a given sample. The effect of experimental conditions can be dramatic, often producing results varying by several hundred percent or even orders of magnitude. For example, Moschopedis, et al. (56) cited VPO MW of asphaltenes ranging from 80,000 to 1000 in the introduction of their paper. Furthermore, Acevedo, et al. (52,55) and Cassani and Eglinton (54) have shown that the apparent MW of asphaltenes can decrease by as much as a factor of 5 after chemical derivatization of polar groups via methylation or reductive alkylation.

Moschopedis, et al. (56), Al-Jarrah and Apitian (57), and McKay, et al. (45) investigated the variation of observed MW with solvent strength. Moschopedis, et al. (56) measured MW in benzene, dibromomethane, pyridine, and nitrobenzene. They found that nitrobenzene yielded the lowest MW and proposed that solvents with high dielectric constants were best suited to VPO. However, McKay, et al. (45) found that MW measured in benzene, tetrahydrofuran (THF), and dichloromethane typically increased in the following order: MW (dichloromethane) << MW (benzene) < MW (THF). For that solvent group, the trend in observed MW did not correlate with that for dielectric constant:

dichloromethane > THF >> benzene. As will be shown later in this work, VPO in THF produces high MW results because of its extensive association with solutes. Furthermore, this property of THF is already widely known; for example, it has served as the basis for group separation of hydroxyaromatics from coal liquids using SEC (61,62) and affects SEC behavior of other types of compounds capable of hydrogen-bonding with THF (43). Apparent VPO MW typically decreases with increasing temperature (56,57), which is consistent with the expectation of less intermolecular association at higher temperatures.

Intermolecular Association

The case of solute-solvent associations is quite simple owing to the essentially constant concentration of solvent(S):

$$K_s = \frac{[MS_x]}{[M][S]^x} \quad (5)$$

$$K'_s = K_s [S]^x = \frac{[MS_x]}{[M]} \quad (6)$$

M = monomeric solute

MS_x = solute-solvent associate

Thus, the ratio of the solute-solvent associate to unassociated solute is effectively constant (K'_s). It should be noted that intermediate associates, MS_{x-1}, MS_{x-2}, etc., were neglected in the above treatment. Also, in cases where solute-solvent association significantly affects VPO measurements, i.e., where K'_s is large, the concentration of MS_x will essentially equal total solute concentration over the concentration range typically employed for VPO measurements.

The impact of solvent-solute association on VPO measurements can be illustrated by the following example. In most modern VPO instruments, π is not measured directly (i.e., as a pressure across a membrane), but indirectly

as a voltage difference (ΔV) between two thermistors--one of which contacts pure solvent and another which contacts the solute-solvent solution. The details of the thermistor cell designs and their theory of operation can typically be found in instrument manuals; e.g., (63). The important point for this discussion is that this type of "osmometer" requires calibration with a pure compound, or a mixture with known $\overline{MW}$, to establish the proportionality between ΔV and π . If the compound or components in the mixture used for calibration do not associate with the solvent to the same extent as the unknowns being measured, a net positive or negative error in $\overline{MW}$, reflecting net contribution to total $\overline{MW}$ by the associated solvent molecules, will result.

Solute-solute association is much more complex because the extent of association depends on the nature of the solutes, their concentration, and the effectiveness of the solvent in dispersing solutes. For the simplest case, dimerization of a pure compound "M", the following relations hold:

$$K_D = \frac{[M_2]}{[M]^2} \quad . \quad (8)$$

The total concentration (g/L) of M (C_T) is simply the sum of the monomeric (C_M) and dimeric (C_{M_2}) species.

$$C_T = C_M + C_{M_2} \quad . \quad (9)$$

The molar concentrations of M and M_2 can be expressed in the form of C (g/L) as follows, given that $MW_{M_2} = 2 MW_M$:

$$[M] = \frac{C_M}{MW_M} \quad , \quad [M_2] = \frac{C_{M_2}}{2MW_M} = \frac{C_T - C_M}{2MW_M} \quad . \quad (10)$$

Expressions in 10 can be substituted into the expression for K_D (equation 8):

$$K_D = \left(\frac{C_T - C_M}{C_M^2} \right) \frac{MW_M}{2} \quad . \quad (11)$$

Equation 11 expressed in a form suitable for its solution via the quadratic formula is shown in equation 12, and the solution is shown in equation 13:

$$2K_D C_M^2 + C_M MW_M - C_T MW_M = 0 . \quad (12)$$

$$C_M = \frac{-MW_M + \sqrt{MW_M^2 + 8K_D MW_M C_T}}{4K_D} . \quad (13)$$

Thus, the concentration of the monomeric species relates to C_T as shown in equation 13.

Individual VPO measurements of MW for a dimerizing substance would reflect $\overline{MW}$ of the monomer and dimer at a given concentration:

$$\overline{MW} = \frac{\sum C_i}{\sum (C_i / MW_i)} = \frac{C_T}{C_M / MW_M + C_{M_2} / 2MW_M} , \quad (14)$$

or, since π/C is proportional to $1/\overline{MW}$:

$$1/\overline{MW} = \frac{C_M / MW_M + C_{M_2} / 2MW_M}{C_T} . \quad (15)$$

Substitution of $1/2(C_T - C_M)$ for C_{M_2} (see equation 9) for the C_{M_2} term in equation 15 yields:

$$1/\overline{MW} = \frac{1}{2MW_M} (C_M / C_T + 1) . \quad (16)$$

Two extreme cases applying to equation 16 should be pointed out. The first is that for very small values K_D , $C_M \approx C_T$ and thus $C_M / C_T \approx 1$. In that case, the effect of dimerization is negligible, as shown in equation 17.

$$1/\overline{MW} = \frac{1}{2MW_M} (1 + 1) = \frac{1}{MW_M} . \quad (17)$$

In the second case, where K_D is very large, $C_M/C_T \approx 0$ and the observed $\overline{MW}$ is twice that of the monomer, as shown in equation 18.

$$1/\overline{MW} = \frac{1}{2MW_M} (0 + 1) = \frac{1}{2MW_M} . \quad (18)$$

For intermediate situations, dependence of C_M on C_T may be calculated via equation 13 and that result substituted into equation 16 to obtain $1/\overline{MW}$ as a function of C_T . This calculation has been performed for a hypothetical dimerizing compound with a monomeric $MW = 400$; curves for three assumed values for K_D are shown in figure 12. It should be noted that since π/C is proportional to $1/\overline{MW}$ (equations 1 and 3), plots of π/C versus C from VPO measurements would assume the same shape as those shown in the figure.

Two features of figure 12 are quite significant. First, at concentrations (C_T) used for the bulk of the VPO measurements in this work (ca. 0.4, 0.8, and 1.4 g/L, see arrows indicated on the figure), linear extrapolation to $C_T = 0$ (see dashed lines on figure) yields erroneously high MW for all values of K_D . However, more typically, even higher concentrations are used for VPO measurements (up to 7 percent w/w, see ref. 54); as apparent in the figure, extrapolated $\overline{MW}$ (i.e., $(\pi/C)_0$) from measurements at higher concentrations would lead to even higher observed $\overline{MW}$ results. In short, linear extrapolation to zero concentration does not adequately correct even for simple solute-solute interactions because of their quadratic dependence on C_T . Formation of trimers and higher associates would cause even greater errors because of their corresponding higher order dependence on concentration. Secondly, because VPO measurements are made at concentrations where the dependence of $1/\overline{MW}$ on C_T is quasilinear (i.e., their parabolic nature is not readily apparent at $C_T > 0.5$ g/L), the appearance of a linear dependence for π/C on C_T as predicted by equation 3 is quite deceptive. Thus, especially at C_T concentrations typically employed for VPO (1-7 weight percent), dimerizing compounds would yield π/C versus C_T plots which would appear linear within experimental error.

FIGURE 12. - Calculated concentration dependence of the reciprocal of apparent molecular weight, i.e., the result which would actually be measured by VPO, for selected values of K_D in the case of a dimerizing substance with a monomeric $MW = 400$ (see text).

Infrared Spectroscopy-A Probe for Intermolecular Association

Intra- and intermolecular hydrogen bonding shifts infrared (IR) bands of affected functional groups to lower frequencies and enhances band intensity (64,65). For this reason, IR spectroscopy was used in this work to obtain supporting data to aid in interpretation of the VPO results.

A major application of IR was estimation of equilibrium constants (K_D) for dimerization of carboxylic acids in 1,2-dichloroethane. IR is especially well suited for this purpose because the carbonyl group in unassociated molecules absorbs near 1750 cm^{-1} , whereas dimerization shifts the carbonyl band to about 1710 cm^{-1} (65,66). Thus, where both free and dimerized species exist, their relative concentration may be estimated from the intensities of the respective IR bands. The appropriate relationship between K_D (equation 8) and IR absorption is derived below.

The major assumption in the IR estimation of K_D , is that the molar absorptivity of the dimeric species (ϵ_{M_2}) is twice that of the monomer (ϵ_M) because of the presence of two carbonyl groups per mole in the dimer; i.e.,

$$\epsilon_{M_2} = 2\epsilon_M. \quad (19)$$

The above assumption is not rigorously correct, because hydrogen bonding typically enhances ϵ . This approximation cannot be too much in error, however, or the varying ratio of monomer/dimer as a function of total carboxylic acid concentration would cause Beers law plots of total absorbance (monomer plus dimer bands) versus total concentration (C_T) to be nonlinear. In fact, Beers law plots for carboxylic acids exhibit a similar degree of linearity to those for other carbonyl-containing compounds. Thus, total absorbance, A_T , is the sum of the absorbance of the monomeric (A_M) and dimeric (A_{M_2}) species:

$$A_T = A_M + A_{M_2}. \quad (20)$$

From Beers law:

$$A_T = \frac{\epsilon_M b C_M}{MW_M} + \frac{\epsilon_{M_2} b C_{M_2}}{MW_{M_2}}. \quad (21)$$

Where b = cell path length and C_M , C_{M_2} , MW_M and MW_{M_2} have the same meaning as in equations 10 and 11. Substitution of $(C_T - C_M)$ for C_{M_2} (equation 9), $2 MW_M$ for MW_{M_2} , and $2\epsilon_M$ for ϵ_{M_2} (equation 19) yields:

$$A_T = \frac{\epsilon_M b C_M}{MW_M} + \frac{2\epsilon_M b (C_T - C_M)}{2MW_M} = \frac{\epsilon_M b C_T}{MW_M} . \quad (22)$$

Equation 22 simply states that total absorbance is linearly related to total concentration, as discussed above. Solving equation 22 for C_T and substitution of it and the analogous expression for C_M into equation 11 results in the following:

$$K_D = \frac{\left(\frac{MW_M A_T}{\epsilon_M b} - \frac{MW_M A_M}{\epsilon_M b} \right) \frac{MW_M}{2}}{\left(\frac{MW_M A_M}{\epsilon_M b} \right)^2} = \left(\frac{A_T}{A_M^2} - \frac{1}{A_M} \right) \frac{\epsilon_M b}{2} . \quad (23)$$

Rearrangement yields:

$$\frac{A_T}{A_M} = \frac{2K_D A_M}{\epsilon_M b} + 1 . \quad (24)$$

Therefore, a plot of A_T/A_M versus A_M should yield a straight line with slope $= 2K_D/\epsilon_M b$ and a y-intercept of 1. Since b is known and ϵ_M may be measured independently, K_D can be determined from IR measurements of A_T and A_M .

Other Methods for $\overline{MW}$ Determination

Nonaqueous titration may be used to determine average equivalent weight ($\overline{EW}$) of an acid or base concentrate. For monoprotic acids or monobasic substances, $\overline{EW} = \overline{MW}$.

$$\overline{EW} = \frac{\text{Sample Weight (mg)}}{\text{mL titrant} \times \underline{N} \text{ titrant}} . \quad (25)$$

Incomplete neutralization or presence of nontitratable material causes the apparent $\overline{EW}$ to be erroneously high; contamination by titratable low MW impurities results in a low apparent $\overline{EW}$.

Equivalent weight (MW if monofunctionality may be assumed) can also be estimated from elemental analysis, if a fraction containing predominantly one compound type is available. For example, for a basic fraction containing only single-nitrogen containing compounds:

$$\overline{EW} = \frac{\text{At. Wt. N} \times 100}{\text{Wt. \% N in fraction}} \cdot \quad (26)$$

Alternately, for an acid fraction containing carboxylic acids:

$$\overline{EW} = \frac{2 \times \text{At. Wt. O} \times 100}{\text{Wt. \% O in fraction}} \cdot \quad (27)$$

Mass spectrometric (MS) methods may be used to calculate either number or weight average MW. Typically, uniform mole sensitivity is assumed. Of course, significant deviation from this ideal behavior can affect the accuracy of the MW result. Also, incomplete volatilization of the sample or other types of instrumental mass-discrimination, as well as MS fragmentation can significantly affect MW results from this approach. From the definition of $\overline{MW}$ (number average):

$$\overline{MW} = \frac{\sum N_i \text{ MW}_i}{\sum N_i} \cdot \quad (28)$$

N_i = number of moles of the "i"th component

Since I_i , the MS intensity of the molecular ion of the "i"th component, is assumed to be equal to N_i as explained above:

$$\overline{MW} = \frac{\sum I_i \text{ MW}_i}{\sum I_i} \cdot \quad (29)$$

MW distributions and $\overline{MW}$ may also be estimated from GC simulated distillation boiling point distributions or average boiling points, respectively. However, this approach is largely restricted to saturate fractions because MW-boiling point correlations are generally unavailable for other compound types, and since the correlation of GC-elution time with boiling point is much less certain for non-saturates. In this work, $\overline{MW}$ was estimated simply by comparing the midboiling point (50 percent off) of a given saturate fraction, as determined by GC simulated distillation (see part A, this chapter), with data for *n*-paraffins calculated by Glinzer (21). The MW

of the *n*-paraffin exhibiting a boiling point nearest to that of midboiling point of the saturate fraction was reported as $\overline{MW}$.

Of course, many other methods are available for determination of MW. Those above are mentioned specifically because they were used in this work to obtain data for comparison to those from VPO.

EXPERIMENTAL, PART B

VPO

A Wescan (Santa Clara, CA) Model 232A thermistor-type osmometer was set up and operated in accordance with operating instructions set forth in the instrument manual. Measurements on pyridine and 1,2-dichloroethane (American Burdick and Jackson, Muskegon, MI) solutions were taken at 85° and 40° C, respectively. Voltage differences (ΔV) between the sample and reference (pure solvent) thermistors were recorded continuously using a strip chart recorder to determine when steady state for ΔV had been achieved. Typically, stabilization for ΔV occurred within 4-10 minutes after introduction of the sample via the syringe supplied with the instrument. All ΔV readings were corrected for "baseline" ΔV which was periodically measured with pure solvent on both thermistors.

Measurements in 1,2-Dichloroethane

Solute concentration was dictated by the $\overline{MW}$ of the material being measured. According to the manufacturer, ΔV readings less than 0.02 mV were unreliable. Thus, it was found that for distillates, even 550-700° C, 0.3 g/L would typically yield ΔV exceeding 0.03 mV; approximately 1 g/L of >700° C residue was required to obtain an equivalent response. Also, according to ASTM D 2503, VPO is not applicable to materials boiling below 220° C. However, because the 200-425° C distillate contained less than 2 weight percent of material boiling below 220° C (see section A), it was deemed suitable for VPO analysis. Measurements were taken at a minimum of three concentrations typically spanning a factor of 5. Except in special cases where the effect of concentration on molecular association was being investigated, the maximum concentration for VPO measurements did not exceed 10 g/L. Linear regression was used to obtain $(\Delta V/c)_0$ from plots of $\Delta v/c$ versus c (equation 3).

Benzil (Aldrich Chemical Co., Milwaukee, WI; MW=210.23) was usually used for calibration of the VPO apparatus. However, *m*-quinquephenyl (MW = 382.51), 5,6-benzoquinoline (MW = 179.22), stearic acid (MW = 284.49), and carbazole (MW = 167.21) were used to cross reference calibration factors based on benzil.

Measurements in Pyridine

More concentrated solutions were required for pyridine VPO measurements in part because the net thermistor response (ΔV) per unit concentration in pyridine was only about one-half that obtained in 1,2-dichloroethane. In addition, measurements at low concentrations were in general more erratic in pyridine. Also, since slightly better agreement between measured and theoretical MW for pure compounds was obtained using *m*-quinquephenyl as the standard rather than benzil, the former was generally employed for calibration.

Thus, concentrations for pyridine VPO typically ranged from 2 to 20 g/L, and occasionally as high as 35 g/L. This concentration range is more typical of that employed in literature work cited earlier. Because of the hygroscopic nature of pyridine, precautions were taken to minimize atmospheric exposure of solvent or solutions. For example, units of g/Kg instead of g/L for concentration of pyridine solutions ($\rho = 0.9832$ g/mL) were usually used because solutions were actually prepared gravimetrically in a nominally moisture-free environment. Otherwise, data handling and general procedures for VPO in pyridine were the same as those specified above for 1,2-dichloroethane.

Infrared Spectroscopy

Infrared spectra were recorded using a dual beam dispersive IR spectrometer (Perkin-Elmer Model 283, Norwalk, CT) using matched 0.5 mm sealed KBr cells.

Nonaqueous Titrations (NAT)

Potentiometric titrations were performed using a Mettler (Hightstown, NJ) automatic titration system comprised of a Model DV10 buret and DK15 control module. Bases were titrated with perchloric acid in acetic anhydride solvent. Details of the procedure appear in Chapter 4 and elsewhere (67).

Acids were titrated with potassium dimethyl sulfoxide. Details of that method are covered in Chapter 3. Methodology for isolation of acid and base concentrates and subfractions is described in Chapters 2-4.

Mass Spectrometry

MW were calculated from low voltage/electron impact/MS (10 eV) of selected fractions as described by Sturm, et al. (68).

RESULTS AND DISCUSSION

Cerro Negro $\overline{MW}$

Table 4 compiles average equivalent and molecular weight data from the various methods on whole distillates, the residue, and chromatographically separated fractions thereof. After critical evaluation of data in table 4, the most self-consistent, and probably most accurate, subset was selected and summarized in table 5 as the best available $\overline{MW}$ for the whole crude and its fractions. The main criteria for selecting "best available" MW results and conclusions from the evaluation are discussed below.

1) In the case of the whole crude, heavy distillates, or the residue, $\overline{MW}$ calculated from analysis of individual fractions of each were selected over those directly determined on the whole materials because in most cases the degree of intermolecular association, which invariably leads to erroneously high $\overline{MW}$, increased with increasing complexity of the sample. For example, $\overline{MW}$ of the $>700^{\circ}\text{C}$ residue computed from data obtained on the individual acid, base, and neutral fractions (996) was significantly lower and in all probability more accurate than either of the directly determined results, 1530 (VPO, $\text{ClCH}_2\text{CH}_2\text{Cl}$) or 2000 (VPO, $\text{C}_5\text{H}_5\text{N}$). However, $\overline{MW}$ determined by VPO on whole neutral fractions in 1,2-dichloroethane solvent were typically lower than those calculated from independent measurements on the corresponding saturate and neutral-aromatic subfractions. Thus, in the latter case, the presence of saturates may actually have minimized intermolecular association between neutral-aromatics. In general, however, more accurate $\overline{MW}$ of complex mixtures are obtained through the fractionation and determination of $\overline{MW}$ on the resulting fractions.

TABLE 4. - Comprehensive listing of average equivalent ($\overline{EW}$, g/equivalent) and molecular ($\overline{MW}$, g/mole) weights for Cerro Negro fractions

Boiling Range, °C	Fraction Type	$\overline{MW}$, VPO ($\text{ClCH}_2\text{CH}_2\text{Cl}$)	$\overline{MW}$, VPO $\text{C}_5\text{H}_5\text{N}$	$\overline{MW}$, MS	$\overline{MW}$, GC Sim. Dis.	$\overline{EW}$ NAT	$\overline{EW}$ Elemental Analysis
<200	Whole Distillate ¹	- ²	-	-	175	-	-
200-425	Whole Distillate	269	-	-	-	-	-
	Whole Acids	294	295	250	-	304	-
	Acids, Subfraction 1	-	-	-	-	252	-
	Acids, Subfraction 2	-	-	-	-	275	-
	Acids, Subfraction 5	-	-	-	-	316	-
	Whole Bases	295	-	289	-	350	-
	Bases, Subfraction 4	-	-	-	-	294	-
	Acids + Bases	370	-	-	-	-	-
	Whole Neutrals	269	-	-	-	-	-
	Saturates	271	-	-	268	-	-
	Neutral-aromatics	260	-	263	-	-	-
425-550	Whole Distillate	400	-	-	-	-	-
	Whole Acids	442	398	341	-	377	-
	Acids, Subfraction 5	-	-	-	-	418	411
	Whole Bases	408	-	400	-	431	-
	Bases, Subfraction 3	-	-	-	-	415	-
	Acids + Bases	411	-	-	-	-	-
	Whole Neutrals	385	-	-	-	-	-
	Saturates	432	-	-	450	-	-
	Neutral-aromatics	356	-	396	-	-	-

¹Wiped-wall still.

²Dash indicates no determination.

TABLE 4. - Comprehensive listing of average equivalent ($\overline{EW}$, g.equivalent) and molecular ($\overline{MW}$, g/mole) weights for Cerro Negro fractions (continued)

Boiling Range, °C	Fraction Type	$\overline{MW}$, VPO ($ClCH_2CH_2Cl$)	$\overline{MW}$, VPO C_5H_5N	$\overline{MW}$, MS	$\overline{MW}$, GC Sim. Dis.	$\overline{EW}$ NAT	$\overline{EW}$ Elemental Analysis
550-700	Whole Distillate	518	649	-	-	-	-
	Whole Acids	542	609	-	-	470	-
	Acid, Subfraction 5	-	-	-	-	472	460
	Whole Bases	559	563	-	-	549	-
	Bases, Subfraction 4	-	-	-	-	529	-
	Acids + Bases	508	-	-	-	-	-
	Whole Neutrals	472	643	-	-	-	-
	Saturates	656	675	-	618	-	-
	Neutral-aromatics	659	650	-	-	-	-
>700	Whole Residue	1530	2000	-	-	-	-
	Strong Acids	1140	2280	-	-	880	-
	Strong Acids, Subfraction 5	-	-	-	-	530	-
	Weak Acids I	970	2450	-	-	-	-
		(2900) ³					
	Weak Acids II ⁴	-	-	-	-	1090	-
	Strong Bases	1610	3760	-	-	1250	-
	Strong Bases, Subfraction 3	-	-	-	-	1110	-
	Weak Base I	1260	2160	-	-	1630	-
	Weak Base II	1320	-	-	-	-	-
	Strong Acids + Strong Bases	1580	-	-	-	-	-
	Whole Neutrals	950	1240	-	-	-	-
	Saturates	682	-	-	688	-	-
	Neutral-aromatics	1420	1230	-	-	-	-

³VPO result for toluene solution.

⁴Incompletely dissolved in $ClCH_2CH_2Cl$ or pyridine.

TABLE 5. - Summary of best available MW data for Cerro Negro fractions and whole crude

Boiling Range, °C	Acids	Bases	Neutrals	Saturates	Neutral Aromatics	Calculated Saturated, Neutral-Aromatic Balance	Calculated Acid, Base, Neutral Balance	Whole Distillate, VPO, $\text{ClCH}_2\text{CH}_2\text{Cl}$	Whole Distillate, VPO, $\text{C}_5\text{H}_5\text{N}$
<200	-	-	-	-	-	-	-	175 ¹	-
200-425	295	298	269	270	26	265	267	269	-
425-550	377	400	385	432	366	379	386	400	-
550-700	470	529	472	656	472 ²	(656) ³	481	518	649
>700, Total	925	1170	950	682	~950 ²	(1210) ³	996	1530	2000
>700, Strong	880	1110							
>700, Weak I	970	1260							
>700, Weak II	1090	1320							
Whole Crude							638	-	-

¹GC - simdis result.

²Estimated from results on whole neutrals.

³Calculated from experimentally measured neutral-aromatic MW.

2) An additional advantage of the fractionation approach for determining $\overline{MW}$ of complex mixtures is that methodology for determining $\overline{MW}$ on resulting fractions can be optimized for each type of fraction. For example, nonaqueous titration (NAT) was found to generally be the method of choice for determining $\overline{MW}$ of acid or base fractions. Furthermore, removal of acids and bases yields a neutral fraction which is much more amenable to VPO analysis than the whole material. In addition, further fractionation of whole acid, base, or neutral concentrates may be used to determine $\overline{MW}$ of a specific compound class within any of those broad groups. Alternately, subfractionation may be used to obtain a class for which $\overline{MW}$ may be measured more accurately than the whole fraction, and therefore the $\overline{MW}$ of the subfraction may be the most accurate measure available for $\overline{MW}$ of the whole acid, base, or neutral concentrate. As discussed below, a $\overline{MW}$ determined on any fraction using an optimized method is typically a better representation of $\overline{MW}$ of the whole material than a directly determined result obtained with a compromise method.

3) In general, relatively small variations in $\overline{MW}$ occurred over acid versus base versus neutral types from a given boiling range. Thus, a result which conflicted with the above generalization was repeated using the same technique and, if possible, cross-checked against an independent technique. For a given distillate, the expected trend in $\overline{MW}$ as a function of type is: saturates > neutral-aromatics > acids/bases (5). However, for Cerro Negro the observed difference in $\overline{MW}$ between types is typically quite small, owing to the following factors: 1) The distributions of each compound class over the entire crude boiling range are not equal. For example, acid and base content increase with AEBP and saturate content decreases with AEBP. Thus, acid and base $\overline{MW}$ are greater than the whole distillate average $\overline{MW}$ in the 200-425° C distillate simply because there is a higher proportion of acids and bases boiling at 425° C than 200° C. Similarly, saturates are actually the lowest $\overline{MW}$ species in the >700° C residue because their distribution effectively ends near 700° C. 2) Azeotropic effects and other nonideal distillation behavior level out $\overline{MW}$ distributions between types. 3) The multiplicity of aromatic structures within the acid, base, and neutral-aromatic fractions further negates differences in AEBP based on structure and/or presence of functional groups in acid or base fractions. For example, carboxylic acids might be expected to exhibit one of the lowest $\overline{MW}$ distributions in a given distillate, given the relatively large increase in AEBP effected by the carboxyl group.

However, since Cerro Negro carboxylic acids are predominantly saturated (see Chapter 3), their $\overline{MW}$ closely resembles that of neutral-aromatics, because the effective increase in AEBP from addition of a carboxyl group to a tricyclic saturate, for example, is approximately the same as obtained from its aromatization to phenanthrene. Although the above hypothetical example is a simplified case, the results in table 5 plus compositional data presented in later chapters generally bear out the concept of greater degrees of saturation in polar compounds relative to neutral-aromatics in a given boiling range, thereby making their $\overline{MW}$ quite similar. 4) At higher boiling ranges, AEBP becomes more dependent on gross structural features such as carbon number and MW, and less affected by functional groups, aromaticity, etc. For example, the range in AEBP between n-hexane (MW = 86, b.p. = 69° C), toluene (MW = 92, b.p. = 111° C), and n-butyric acid (MW = 88, b.p. = 162° C) is significantly greater than between n-eicosane (C₂₀H₄₂, MW = 282, b.p. = 343° C), n-pentadecylbenzene (C₂₁H₃₆, MW = 288, b.p. = 373° C), and stearic acid (C₁₈H₃₆O₂, MW = 284, b.p. = 370° C) (20,69). In fact, if these three series, i.e., n-alkanes, n-alkylbenzenes, and n-alkanoic acids, were taken to sufficiently high carbon numbers, their AEBP for a given MW would converge. The above four effects account for the general agreement between $\overline{MW}$ of acids, bases, and neutrals in each boiling range, and preliminary data indicating gross differences in $\overline{MW}$ between types were usually found to be in error.

In conclusion, $\overline{MW}$ for Cerro Negro crude and >700° C resid were found to be 638 and 996, respectively. Data in table 5 certainly represent some of the lowest $\overline{MW}$ reported for heavy oils and their fractions, although the trend in literature $\overline{MW}$ for petroleums and petroleum fractions is clearly downward. For example, in 1985 Acevedo, et al. (52), reported the $\overline{MW}$ of a Cerro Negro asphaltene fraction to be near 2000. That result and their corresponding ones for other heavy oils were significantly lower than most earlier data, and were obtained only after careful experimental design to minimize molecular associations. However, the same group has more recently suggested a $\overline{MW}$ of 1200 (a decrease of nearly 50 percent) for the same Cerro Negro asphaltene (55). Moreover, their latest result and $\overline{MW}$ reported here are in all probability still too high, because of the great difficulty in elimination of all association effects. Furthermore, MW distributions from field ionization MS corroborate lower MW from this work. For example, two independent studies indicate the upper limit of MW in petroleum residues to be near 2000 (5,45). Thus,

earlier $\overline{MW}$ data as well as some fairly recent results ranging in the tens of thousands are clearly gross overestimates. The estimates for $\overline{MW}$ obtained here indicate average carbon numbers of ca. 45 and 70 for the whole crude and >700° C residue, respectively. This carbon number/ $\overline{MW}$ range is more consistent with 1) formation of a fluid, homogenous oil phase, 2) reservoir displacement during production, and 3) other chemical/physical properties in section A, than prior estimates indicating large macromolecules.

Methodology for Determination of $\overline{MW}$

As table 4 shows, six different methods or variations were applied to determining $\overline{MW}$. This section discusses individual data in table 4 in more detail and outlines the strengths and limitations of each method.

MS Determination of $\overline{MW}$

In this work, no attempt was made to apply MS methods to marginally volatile samples, or employ unconventional sample introduction or ionization approaches. Thus, uncertainties or controversies often raised to the above issues do not apply here. The major point addressed below is the assumption of uniform mole sensitivity discussed earlier, and its impact on $\overline{MW}$ results.

The general conclusions derived from this work regarding the validity of the above assumption and overall accuracy of low voltage/electron impact/MS-derived (LV/EI/MS) $\overline{MW}$ are: 1) on totally aromatic samples, accurate $\overline{MW}$ are obtained with the assumption of equal mole sensitivity, and 2) if a significant proportion of nonaromatic material is present, inaccurate $\overline{MW}$ may result. For example, the MS result for the 200-425° C whole acids (table 4) clearly shows the inapplicability of LV/EI/MS for samples containing significant quantities of nonaromatic carboxylic acids (see previous section). In that sample, the weaker aromatic acids (e.g., benzologs of pyrrole and hydroxyaromatics) clearly exhibited lower MW distributions than the carboxylic acids. Thus, the MS $\overline{MW}$ is erroneously low for that fraction because the carboxylic acids, which comprised about 60 weight percent of the whole acids (see Chapter 3), were largely undetected by LV/EI/MS. The impact of this error on the MS $\overline{MW}$ for 425-550° C acids was slightly less because of the lower proportion of carboxylic acids in that boiling range. For base and neutral-aromatic fractions, generally good agreement between MS and other methods was obtained. Good agreement between VPO and GC/MS $\overline{MW}$ on low MW fractions has been reported previously (38).

The unsuitability of LV/EI/MS for saturated compounds is widely recognized, and the above discussion was not intended to imply any novelty in that respect. However, both the prevalence of carboxylic acids in acid concentrates from Cerro Negro and their apparent dissimilarity in MW distribution compared to those of other acidic classes merit mention.

GC Determination of $\overline{MW}$ for Saturates

Agreement between VPO results and $\overline{MW}$ for saturates calculated from GC-simulated distribution profiles was surprisingly close (table 4), especially considering that the GC method is calibrated using *n*-paraffins, whereas Cerro Negro saturate fractions contain virtually 100 percent naphthenic types (see Part A of this Chapter and Chapter 2). Generally, VPO and GC results agreed within one methylene group (14 mass units). Considering its significantly shorter analysis time and the fact that it is highly automated, the GC method is preferred for determining MW as well as boiling point distributions for saturate fractions.

Equivalent Weight Methods

NAT and elemental methods for determining $\overline{EW}$ are grouped here for purposes of discussion because analogous assumptions and potential errors are involved in the application of either toward determining $\overline{MW}$.

Unfortunately, use of elemental composition to calculate $\overline{EW}$ was limited to a relatively few fractions meeting the following conditions: 1) reliable elemental data must be available, 2) the stoichiometry of the heteroatom(s) present must be known, and 3) contaminants, especially those containing the heteroatom providing the basis for calculating $\overline{EW}$, must be absent. The major limitation in this work was simply the lack of elemental data (see later chapters), especially for acid and base subfractions where conditions 2 and 3 could be reasonably met. However, calculated $\overline{EW}$ for subfraction 5, which contains predominantly carboxylic acids, from the 200-425° C and 425-550° C acids agreed well with $\overline{EW}$ from NAT (table 4). Elemental data were available for whole acid and base concentrates, for example (see Chapter 2), but conditions 2 and 3 above are not met for such crude fractions. Thus, a more extensive effort is needed to fully evaluate this approach.

Overall, NAT proved to be the method of choice for determining $\overline{EW}$ of acid and base fractions. Also, in most cases, $\overline{EW}$ equaled $\overline{MW}$. The unequal distribution of $\overline{EW}$ among acid subfractions, mentioned earlier in connection with Cerro Negro $\overline{MW}$ and MS methodology, is clearly evident in NAT data. For example, table 4 $\overline{EW}$ of subfractions 1 and 2, which contain predominantly pyrrolic benzologs and other weakly acidic types, from the 200-425° C acids closely matched the MS result for $\overline{MW}$. The observed agreement between $\overline{EW}$ for subfractions containing predominantly aromatic species and the MS-derived $\overline{MW}$ for whole acids further substantiates earlier points, i.e., 1) that the MS-derived $\overline{MW}$ for whole acids are too low because carboxylic acids were largely undetected, 2) that the $\overline{MW}$ distribution of carboxylic versus noncarboxylic aromatic acids differed significantly in the 200-425° C and 425-550° C distillates, and 3) that the NAT $\overline{EW}$ for whole acids, which represents the weighted average of all acidic types, represents the best available result for $\overline{MW}$.

Interestingly, the NAT $\overline{EW}$ for the whole 550-700° C acids closely matched $\overline{EW}$'s for the corresponding carboxylic acid subfraction (subfraction 5, table 4). However, this observation is consistent with points made earlier concerning increased equalization of $\overline{MW}$ between different chemical types at increasing $\overline{MW}$ or boiling point due to extensive alkylation and other leveling effects. On the other hand, subfraction 5 from the >700° C strong acids exhibited a much lower $\overline{EW}$ than the whole strong acids. The trend in >700° C $\overline{EW}$ may be explained either by 1) the presence of multiply-titrated compounds or 2) preferential elution of relatively polar, small $\overline{MW}$, compounds in subfraction 5. Overall, the NAT $\overline{EW}$ for whole strong and weak acids were consistent with $\overline{MW}$ for other fractions.

Interpretation of NAT results for base fractions and subfractions was necessarily different than that for acids. The titrant used for acids, potassium dimsyl, is a sufficiently strong base that virtually any petroleum-derived acidic species can be titrated (see Chapter 3). However, the titrant for bases, perchloric acid, is of insufficient acidity to titrate selected very weak bases in petroleum (see Chapter 4). For example, $\overline{EW}$ for whole base

concentrates are typically high by ca. 10 percent; also, subfraction 1's from bases are often only 50 percent titrated because that subfraction typically contains the highest proportion of very weak bases. Thus, in the case of bases, the $\overline{EW}$ determined for a relatively basic subfraction was typically taken to represent that of the whole base concentrate. Given the differences in $\overline{EW}$ observed for the acidic subfractions, this assumption obviously cannot be rigorously justified, but the $\overline{EW}$ determined on a subfraction which can be completely titrated is probably a better estimate of $\overline{EW}$ for the whole bases than a directly determined $\overline{EW}$ which is known to be too high. In any case, the difference in $\overline{EW}$ between the whole bases and subfraction 3 or 4 was typically 10 percent or less. In addition, a study of $\overline{EW}$ versus subfraction number, analogous to that done for acids, clearly was not feasible because of the incomplete titration of very weak bases.

VPO in 1,2-Dichloroethane and Pyridine

Because of their extensive utilization in the industry and nominally universal applicability, VPO methods underwent the most extensive evaluation of all MW methods examined. Salient conclusions from the VPO study are summarized below.

1. For whole distillates boiling below 550° C and their fractions, VPO in either solvent generally yielded results of acceptable accuracy. However, two exceptions to the above bear mentioning: 1) the 425-550° C acids, where the pyridine result was clearly superior, and 2) measurements of 1:1 blends of 200-425° C acids plus bases in 1,2-dichloroethane, which yielded a combined $\overline{MW}$ higher than either of the individual fractions.
2. For the 550-700° C distillate, the >700° C residue, and their fractions, 1,2-dichloroethane generally out performed pyridine as a VPO solvent, except for 550-700° C saturates, neutral-aromatics, and bases, where measurements in the two solvents agreed.
3. For the residue, acceptable VPO results were obtained only on saturate and whole neutral fractions. The results here concur with statements made in many of the papers cited in the Introduction; i.e., that problems in application of VPO to residues or "asphaltene" fractions are much more severe than encountered with distillates.

4. The major source of error in 1,2-dichloroethane VPO is solute intermolecular association, whereas solvent-solute interactions cause most of the inaccuracy in pyridine VPO.
5. The presence of functional groups, e.g., those in acidic or basic compounds, is **not** a necessary prerequisite for solute-solute or solute-solvent interactions. For example, neutral-aromatic fractions exhibited both types of interactions. Furthermore, pyridine associated more with basic fractions, especially the $>700^{\circ}\text{C}$ strong bases, than with acids. In contrast, a simple acid-base pairing model would predict greater association of pyridine with acidic solutes. The observed trend over all VPO data was generally more consistent with aromatic-ring interactions predominating over associations involving functional groups.
6. The best accuracy with VPO is achieved using the most dilute solutions consistent with the sensitivity of a given instrument on fractions free of acidic or basic compounds. In general, chlorinated solvents represent the best compromise between minimizing solute-solute interactions and avoiding strong solute-solvent interactions.
7. The extent and type of intermolecular association affecting the observed $\overline{MW}$ are often revealed by the dependence of osmotic pressure on concentration. For example, zero dependence of $\Delta V/C$ (ΔV is proportional to π) vs C_T usually indicates maximum association at all values of C_T . Non-associating solutes such as saturates usually show a low, yet non-zero dependence for $\Delta V/C_T$ vs C_T ; partial association results in parabolic shaped curves.

Numerical data in table 4, plots of VPO data corresponding to equation 3, and infrared studies of intermolecular association (see next section) form the basis for the above conclusions.

Correlation of plots of raw VPO data corresponding to equation 3, i.e., extrapolation to determine osmotic pressure at infinite dilution, with final results in table 4 revealed several significant points. Figures 13-15 show representative plots of $\Delta V/C_T$ vs C_T ($\Delta V \propto \pi$) for determining $(\Delta V/C_T)_0$ of 200-425° C fractions in 1,2-dichloroethane (figure 13), 550-700° C fractions in 1,2-dichloroethane (figure 14), and selected fractions over all boiling ranges

in pyridine (figure 15). In addition, figure 16 compares 1,2-dichloroethane curves for neutral concentrates from the Cerro Negro residue with those from two other heavy oils.

Saturate fractions exhibited ideal VPO behavior in all boiling ranges and in either solvent. Hence, curves for saturates in figures 13-15 all exhibit very good linearity and slightly negative slopes corresponding to a negative value for A_2 in equation 3. As previously mentioned, good correlation between $\overline{MW}$ for saturates determined by VPO and GC methods was obtained. Thus, the plots for saturates serve as baselines for ideal VPO behavior.

Curves for most of the 200-425° C fractions and the whole distillate in figure 13 share a common shape; they are quasilinear at $C_T > 0.5$ g/L and approximately level at $C_T < 0.5$ g/L. Thus, the observed trend in $\Delta V/C_T$ versus C_T for this boiling range is inconsistent with equation 3 as well as the later relations developed in the theory section which predict curves analogous to those in figure 12. The nonlinear response at $C_T < 0.5$ may reflect imperfect baseline compensation or some other instrumental artifact although the effect is not apparent in data for the saturate fraction, which is linear. In reality, no adequate explanation for this effect was apparent. In practice, however, the impact of the nonlinearity was minimal, since most of the results derived from these plots (table 4) agreed well with those from other methods and were self-consistent (table 5). Conversely, the plot for the 1:1 blend of acids and bases showed virtually no dependence on total concentration (C_T). As will become increasingly evident during the consideration of analogous curves below, zero dependence of $\Delta V/C_T$ on C_T almost always indicates maximum intermolecular association at all values of C_T examined. Thus, a strong interaction between 200-425° C acids and bases is indicated; this conclusion is further supported by their much higher combined apparent $\overline{MW}$ (370), compared to results obtained on the separate fractions (295 and 298, table 5).

FIGURE 13. - Actual concentration dependence of the reciprocal of apparent molecular weight ($\Delta V/C \propto 1/\overline{MW}$) for Cerro Negro 200-425° C fractions in 1,2-dichloroethane.

FIGURE 14. - Actual concentration dependence of the reciprocal of apparent molecular weight ($\Delta V/C \propto 1/MW$) for Cerro Negro 550-700° C fractions in 1,2-dichloroethane.

FIGURE 15. - Actual concentration dependence of the reciprocal of apparent molecular weight ($\Delta V/C \propto 1/\overline{MW}$) for selected Cerro Negro fractions in pyridine.

FIGURE 16. - Comparative VPO curves obtained in 1,2-dichloroethane for neutral fractions from three heavy oils.

With the exception of the 550-700° C bases, which showed the same anomalous behavior noted earlier for 200-425° C fractions, the majority of the fractions in figure 14 exhibited behavior qualitatively consistent with concentration dependent intermolecular association; e.g., figure 12. Furthermore, MW calculated from curves in figure 14 exhibiting the parabolic dependence of $\Delta V/C_T$ on C_T predicted by equations 13 and 16 were invariably higher than "best available" $\overline{MW}$ determined by other methods summarized in table 5. Thus, results for several of the 550-700° C fractions and the whole distillate support theoretical concepts derived earlier concerning 1) nonlinear dependence of π/C_T vs C_T in cases where dimerization or formation of higher associates occurs and 2) the inability of linear extrapolation to accurately compensate for such effects. Moreover, these effects were all magnified in the corresponding plots for >700° C fractions (not shown).

Interestingly, the 1:1 blend of 550-700° C acids plus bases exhibited a relatively "ideal" type of curve resembling that of the saturates much more than those of the individual fractions. Furthermore, the $\overline{MW}$ of the acid-base mixture, 508, was lower than VPO results obtained for either fraction by itself and in turn agreed well with the weighted average of "best available" MW for 550-700° C acids and bases determined by NAT (table 5). As noted above, the corresponding data from 200-425° C fractions showed exactly the opposite trend. Results for 425-550° C acids, bases, and 1:1 acids:bases were intermediate between those of the 200-425° C and 550-700° C fractions, and corresponding data for >700° C fractions were all erroneously high. Taken at face value, these results indicate: 1) significant acid-base pairing for low-boiling (low $\overline{MW}$) compounds which diminishes with increasing $\overline{MW}$ due to increasing steric hindrance or other structural effects; 2) increasing association within members of a given general type, e.g., acids, with increasing $\overline{MW}$; 3) relatively strong association of nondistillable compounds regardless of type; and 4) dispersive as well as associative interactions.

The dispersive effect, i.e., the ability of one compound class to disrupt intermolecular associations within a given class or between two different classes, is also evident in the results for 550-700° C whole neutrals versus neutral-aromatics. $\overline{MW}$ for whole neutrals determined in 1,2-dichloroethane was 472; results for the corresponding saturate and neutral-aromatic subfractions were 656 and 659, respectively. The relatively high $\overline{MW}$ for saturates is

consistent with trends in MW for other distillates and the mid-boiling range point for the distillate (625° C). However, the $\overline{MW}$ for neutral-aromatics should obviously be <472 to obtain a saturate/neutral-aromatic balance consistent with the MW of whole neutrals. As shown in figure 14, the average of three independent determinations of the 550-700° C neutral-aromatics indicated essentially zero dependence of $\Delta V/C_T$ on C_T . As mentioned above, this behavior is characteristic of maximum intermolecular association at all measured values of C_T . Thus, saturates apparently possess a dispersive property for decreasing the association of 550-700° C neutral-aromatics in an analogous manner to that discussed above for 550-700° C acids and bases. Furthermore, the >700° C saturates exhibited the same effect on >700° C neutrals. However, none of these dispersive effects was apparent in pyridine VPO measurements. In pyridine, higher results for whole neutrals, commensurate with those of neutral-aromatics, were obtained.

As for 1,2-dichloroethane, the dependence of $\Delta V/C_T$ on C_T in pyridine varied significantly as a function of fraction type and boiling range. Figure 15 shows representative results. The 550-700° C saturate curve and $\overline{MW}$ obtained in pyridine were quite similar to the 1,2-dichloroethane results. Also, in the case of 550-700° C bases, where $\overline{MW}$ in the two solvents agreed and closely matched the NAT result (table 4), the pyridine plot exhibited good linearity and a negative slope. However, curves for other fractions generally differed significantly from one solvent to the other. For example, curves for 200-425° C and 425-550° C acids typically exhibited better linearity in pyridine, and the resulting $\overline{MW}$ was equal in the two solvents for the 200-425° C acids and lower in pyridine for the 425-550° C acids. On the other hand, pyridine curves for virtually all 550-700° C and >700° C fractions exhibited zero or slightly positive slopes as shown for the 550-700° C acids, >700° C neutrals, and >700° C whole residue in the figure. As mentioned earlier, this pattern typically indicates strong association effects. Furthermore, the $\overline{MW}$ calculated from these curves invariably exceeded those determined in 1,2-dichloroethane, by a factor of 2 in some cases.

In part because of the work by Moschopedis and coworkers (56) and numerous later applications of their methodology, e.g. (70), pyridine has become widely used as a VPO solvent. Its strong solvating power has undoubtedly also contributed to its popularity, especially for asphaltenes and like materials.

In addition, $\overline{MW}$ measured in pyridine are lower than obtained in many solvents; e.g., benzene.* However, the effect of the extensive association between pyridine and many types of solutes on the observed $\overline{MW}$ is not widely recognized. Both the high $\overline{MW}$ for high-boiling Cerro Negro fractions determined in pyridine and the typical zero or slightly positive dependence of $\Delta V/C_T$ on C_T usually indicate extensive association between pyridine and solutes, rather than ideal behavior as is often assumed. Indeed, this effect largely accounts for its strong solvating power. Thus, as pointed out earlier in the discussion of VPO theory, the excellent linearity typically observed during extrapolation of pyridine VPO data to infinite dilution generally signals that the $\overline{MW}$ of a pyridine-solute associate, rather than that of the solute alone, is being measured. Based on the results obtained here, the contribution of associated pyridine molecules to $\overline{MW}$ can even exceed 1000 daltons, which is equivalent to over 12 pyridine molecules per solute.

Figure 16 compares 1,2-dichloroethane VPO plots of resid neutral concentrates from Cerro Negro, Wilmington, and Mayan heavy oils. General inspection properties of the latter two oils were given in table 3, section A of this report. The Cerro Negro $>700^\circ \text{C}$ neutrals exhibit a much stronger dependence of $\Delta V/C_T$ on C_T . However, the equivalent $\overline{MW}$ calculated for a Cerro Negro " $>550^\circ \text{C}$ " neutral concentrate, 846, is only 10-20 percent higher than for the other oils. The similar results obtained for $\overline{MW}$ contradict the concept of widely varying MW distributions for oils of varying origin; the greater slope in the Cerro Negro data indicates significantly stronger intermolecular association among its constituents.

Optimizing Methodology for Determining $\overline{MW}$ for Heavy Oils

Given the impracticability of performing the extensive study of $\overline{MW}$ described here on a routine basis to determine $\overline{MW}$ of a given whole heavy oil or fractions thereof, a streamlined procedure is clearly needed. On the other hand, indiscriminate VPO measurements on whole crudes or gross fractions thereof are not acceptable either, since the results would reflect an unknown combination of the actual $\overline{MW}$'s and association tendencies of each sample (71).

*In this work, only one $\overline{MW}$ was determined in toluene (table 4); given the relatively high $\overline{MW}$ obtained and zero dependence of $\Delta V/C_T$ on C_T , benzene or toluene were excluded from further consideration as VPO solvents.

A suggested approach, which will require additional verification, is VPO determination of $\overline{MW}$ on the neutral fraction from a given oil. Although this approach requires the assumption of equal $\overline{MW}$ for acidic, basic, and neutral types, it carries the inherent advantage of experimental viability. That is, neutral fractions are easily obtained (see Chapter 2) and their $\overline{MW}$ can be determined with reasonable accuracy by VPO. Stated simply, an accurate measure of $\overline{MW}$ for a portion of each heavy oil is of greater value than an inaccurate determination on the whole oil.

Where determination of $\overline{MW}$ on acidic or basic components is the prime interest, titration appears to be the only viable technique especially for high-boiling or nondistillable fractions. Although this approach requires the assumption that $\overline{EW} = \overline{MW}$, the maximum probable error incurred from this assumption is far less than known errors in other methods. Additional experimental development of NAI methods would probably improve the correspondence between $\overline{EW}$ and $\overline{MW}$.

Intermolecular Association

Although intermolecular associations have been previously discussed in conjunction with distillations (part A), Cerro Negro $\overline{MW}$, and MW methodology, their overall effect on physical properties--including viscosity, apparent $\overline{MW}$, and even specific gravity--is great enough to warrant a separate section for their evaluation and summary.

In general, results presented earlier are best explained by an association model based on charge-transfer interactions between aromatic moieties. In this model, functional groups influence intermolecular association, not by direct interaction, but rather by affecting the electron donor/acceptor properties of aromatic systems. For example, neutral-aromatics were chromatographically separated into aromatic ring-number fractions (see Chapter 5A) based on the increasing strength of association with the stationary phase, which is based on a dinitrobenzene derivative which functions as an electron acceptor, with increasing aromatic-ring size. Thus, intermolecular association of Cerro Negro fractions may be explained in an analogous manner to that of the charge-transfer chromatographic separation:

- 1) The general increase in association effects with $AEBP/\overline{MW}$ is consistent with the corresponding increase in average size of aromatic nuclei with AEBP.
- 2)

Heteroatoms may impart electron donating or accepting properties to aromatic systems, depending on their chemical form. Thus, the general effect of higher levels of heteroatomic species in higher AEBP/ $\overline{MW}$ fractions is to increase association by enhancing electron donating properties of some species and acceptor properties in others. 3) The extensive association of pyridine during VPO experiments with high-boiling or nondistillable fractions may be similarly explained. For example, if the association had occurred via specific interaction of pyridine with acidic functional groups, errors in VPO $\overline{MW}$ for 200-425° C acids would have exceeded those for >700° C acids, since the effect of pairing one or more pyridines to a given functional group on a small molecule produces a greater relative increase in $\overline{MW}$ than for a large molecule. In reality, $\overline{MW}$ for low-boiling fractions in pyridine were more accurate than those for high-boiling fractions. Therefore, the charge-transfer mechanism is consistent with the more extensive interaction with pyridine observed with increasing $\overline{MW}$ of a given fraction. 4) Finally, the significant association observed for neutral-aromatics can only be explained by interactions between aromatic systems because of the absence of polar functional groups in that fraction.

Yen (72) proposed charge-transfer interactions earlier for petroleum residues based on infrared evidence. Quinga and Larsen (73) have recently suggested that London dispersion forces between polynuclear aromatics in part account for the solid structure of high rank coal. Results obtained here are consistent with charge-transfer and/or London dispersion interactions. The main point raised is that hydrogen-bonding interactions, although not excluded in this model, are not the dominant interaction mechanism as is typically assumed.

As discussed in the theory section, infrared spectroscopy (IR) was used to study hydrogen-bonding of acidic functional groups in order to obtain supporting information for the VPO studies. Figure 17 shows the portion of the IR of 1,2,3,4-tetrahydrocarbazole where the N-H stretching band occurs. In carbon tetrachloride, a relatively weak solvent, bands corresponding to both monomeric (3492 cm^{-1}) and dimeric species (3428 cm^{-1}) are observed at concentrations >5 mg/mL. However, in 1,2-dichloroethane or tetrahydrofuran (THF) no evidence of dimeric species was observed. The monomeric band in THF

was shifted to a significantly lower frequency, 3320 cm^{-1} and only slightly in 1,2-dichloroethane, 3460 cm^{-1} . Behavior of N-H bands in Cerro Negro acids closely paralleled that of tetrahydrocarbazole.

Figure 18 shows the analogous shift in frequency and band broadening for the O-H band of m-cresol in the same three solvents. Unlike 1,2,3,4-tetrahydrocarbazole, associated phenols do not give rise to a distinct secondary band, but rather a very broad band spanning from ca. 3500 to 3100 cm^{-1} due to the variety of associates formed (74). A small band corresponding to self-associated m-cresol appears in spectra taken in both chlorinated solvents. The O-H group is extensively associated with THF, and the resulting IR band broadens significantly, increases in relative intensity, and shifts to lower wavenumber. These effects have been previously noted for O-H and N-H compounds in IR spectra of coal liquids obtained in THF (75).

The association of carboxylic acids is similarly reflected in the IR spectral region corresponding to absorption by carbonyl functionalities. Figure 19 shows spectra of n-decanoic and Cerro Negro 200-425° C acids in 1,2-dichloroethane, and figure 20 shows n-decanoic acid in carbon tetrachloride and THF. In 1,2-dichloroethane, both the Cerro Negro and n-decanoic acids exist in monomeric (1750 cm^{-1}) and dimeric (1710 cm^{-1}) forms. The molar ratio for monomeric and dimeric forms is concentration dependent, as evident in figure 19 and described by equations 13 and 16. In carbon tetrachloride, n decanoic acid exists almost entirely as dimeric species, which correlates with previous spectra showing higher degrees of association in that solvent. In THF, extensive THF solvation effectively prevents dimerization; a single band at 1739 cm^{-1} is observed. This effect is also consistent with prior THF spectra indicating replacement of solute-solute interactions with solute-solvent interactions.

Unfortunately, it was not possible to obtain corresponding spectra in pyridine with the available instrumentation because of its high background absorption in spectral regions investigated. Use of pyridine would require a Fourier transform spectrophotometer. Spectra obtained in THF may be indicative of those in pyridine, because of their generally similar properties and similar association effects observed with either as an eluent in size exclusion chromatography, for example (76); yet equivalence, in terms of the extent and mechanism of association, cannot be assumed.

FIGURE 17. - Partial IR spectra of 1,2,3,4-tetrahydrocarbazole in carbon tetrachloride at the indicated concentrations (mg/mL). Note the increasing intensity of the N-H band corresponding to the dimeric species (3428 cm^{-1}) relative to that of the monomeric species (3492 cm^{-1}) with increasing concentration.

FIGURE 18. - Partial IR spectra of *m*-cresol showing frequency and intensity of O-H band as a function of solvent polarity. Concentrations (mg/mL) and wavenumbers (cm⁻¹) were: 5.71, 3620 (CCl₄); 5.27, 3570 (ClCH₂CH₂Cl); and 10.2, 3310 (THF), respectively.

FIGURE 19. - Partial IR spectra of *n*-decanoic acid (A) and Cerro Negro 200-425° C acids (B) showing effect of concentration (mg/mL in 1,2-dichloroethane) indicated for each spectrum, on the relative intensity of carbonyl bands corresponding to monomeric (1750 cm^{-1}) and dimeric (1710 cm^{-1}) carboxylic acids.

FIGURE 20. - Partial IR spectra of *n*-decanoic acid showing carbonyl bands as a function of concentration (mg/mL) in carbon tetrachloride (A) and THF (B). Note the greatly decreased intensity of the band corresponding to monomeric (1760 cm^{-1}) relative to dimeric species (1712 cm^{-1}) in (A) compared to Fig. 19 (A). Note also the appearance of a single band in (B) 1739 cm^{-1} corresponding to a monomeric, THF solvated species.

Figure 21 shows the rather minimal IR effect of adding a nearly three-fold molar excess of quinoline to a 1,2-dichloroethane solution of *p*-toluic acid. The ratio of monomeric to dimeric species is nearly the same with and without quinoline, but the intensity of both bands is depressed by quinoline. Analogous spectra of more dilute *p*-toluic acid solutions showed a more pronounced decrease in monomeric species relative to dimeric species in the presence of quinoline. Corresponding effects of quinoline on the free O-H band (3480 cm^{-1}) were also observed. Overall, the magnitude of acid-base interactions indicated in figure 21 and other IR work with pure compounds and low-boiling Cerro Negro fractions was qualitatively consistent with the modest increase in VPO $\overline{MW}$ for the 1:1 mixtures of acids and bases shown in table 4. As noted earlier, the largest effect obtained was a 25 percent increase in apparent $\overline{MW}$ for 200-425° C acids + bases. For higher boiling acids and bases, association as indicated by VPO $\overline{MW}$ within individual acidic or basic fractions was essentially equal to that for 1:1 mixture of acids and bases. Therefore, although acid-base or other types of pairing could account for relatively small increases in apparent $\overline{MW}$, the extensive association indicated by VPO measurements on >700° C fractions is totally inconsistent with a functional group-based association mechanism.

As discussed earlier in the theory section, IR measurements may be used to determine equilibrium constants for detectable intermolecular associations; i.e., primarily those involving hydrogen bonding. Also, since carboxylic acids predominantly form dimers, equation 24 is appropriate for determining K for dimerization. As the reader may recall, the main assumption in the derivation of equation 24 was equal IR response for hydrogen-bonded and free carbonyl groups. The essentially linear response for pure carboxylic acids shown in figure 22 and corresponding ones for Cerro Negro fractions containing carboxylic acids supports that assumption. For example, the ratio of monomeric/dimeric IR bands over concentrations indicated in figure 22 ranged well over an order of magnitude; yet total IR absorbance versus total concentration yielded a linear relationship in accordance with Beer's law.

FIGURE 21. - Partial IR spectra of *p*-toluic acid (0.97 mg/mL in 1,2-dichloroethane) with and without the presence of quinoline (molar ratio of *p*-toluic acid/quinoline = 0.36). Band frequencies for *p*-toluic acid are 1732 (monomer) and 1697 (dimer) cm⁻¹.

**DO NOT MICROFILM
THIS PAGE**

CHAPTER 2

FIGURE 22. - Beer's law plots for total IR absorbance of carboxylic acid monomer plus dimer carbonyl bands vs concentration.

Figure 23 shows plots corresponding to equation 24 for pure carboxylic acids (A) and Cerro Negro fractions (B). As discussed later in Chapter 3, acid subfraction 5 contains the bulk of the carboxylic acids present in each whole acid concentrate. Significantly, all curves shown in the figure yield a y-intercept of 1 within experimental error, in accordance with equation 24. That result plus the degree of linearity obtained demonstrate the applicability of equation 24.

Table 6 summarizes IR molar absorptivities from Beer's law plots of carbonyl absorption such as those in figure 22, dimerization constants calculated from slopes of figure 23 plots, and the results of calculations assessing the effective error in VPO $\overline{MW}$ resulting from carboxylic acid dimerization. Molar absorptivities of the pure carboxylic acids were significantly higher than those determined for the Cerro Negro carboxylic acid concentrates (subfraction 5). This discrepancy probably resulted from inherent structural differences between Cerro Negro acids versus the three relatively simple compounds selected. Alternately, contamination of the Cerro Negro fractions by other compound types may have caused their measured ϵ_M to be erroneously low. The higher response of p-toluic versus the pure saturated carboxylic acids is typical (see Chapter 3), and serves as an example of the effect of structure on carbonyl band intensity. The nominal cell path length, 0.5mm, was assumed for all ϵ_M calculations. For Cerro Negro fractions, $\overline{EW}$ determined by NAT was used in the calculation of ϵ_M .

As shown in equation 24, the slope of plots in figure 23 was equal to $2K_D/\epsilon_M b$; thus ϵ_M was required for calculation of K_D . In the case of Cerro Negro fractions, the average ϵ_M for all boiling ranges was used in conjunction with the slope of all points in figure 23(B) to obtain an average K_D for all boiling ranges. This result was only slightly lower than that obtained for the pure saturated carboxylic acids; p-toluic acid gave rise to a moderately higher K_D . However, the overall magnitude of all K_D data clearly indicates that dimerization in 1,2-dichloroethane is a much weaker interaction than formation of most aqueous metal-ligand complexes, for example.

FIGURE 23. - Plots corresponding to equation 24 for determining equilibrium constants for dimerization of carboxylic acids (see text).

Results for K_D were substituted into equation 13 for calculation of C_M , which was in turn used to calculate $1/\overline{MW}$ via equation 16. For simplicity, the previously discussed variation in $\overline{MW}$ between carboxylic acids and other acidic types was ignored and the "best available" $\overline{MW}$ shown in table 5 were used in the calculations. The effect of this simplification was negligible as shown below. Figure 24 shows the calculated dependence of the reciprocal of "apparent" $\overline{MW}$, i.e., the weighted average of monomeric and dimeric species, on C_T . The curve for cyclopentane carboxylic acid, the pure compound with the closest K_D to that of the Cerro Negro acids, is also shown in the figure.

Strictly speaking, C_T in figure 24 refers only to carboxylic acid types, since infrared spectra (see above) indicated minimal association of other types in 1,2-dichloroethane. However, for the purpose of calculating the maximum error in VPO $\overline{MW}$ resulting from functional group-based associations, the association of other types was assumed to equal that of carboxylic acids. Also, for comparison purposes, it was assumed that VPO measurements were obtained at 0.3, 0.6, and 1.5 g/L for all Cerro Negro fractions and pure compounds. Given those assumptions, the "apparent" VPO $\overline{MW}$ calculated from linear regression of $1/\overline{MW}$ at C_T 's listed above was typically only 20 g/mole higher than the correct value; the relative error in $\overline{MW}$ actually decreased with increasing AEBP/ $\overline{MW}$ of the Cerro Negro fractions (table 6). Of course, had points corresponding to higher C_T values been selected, higher apparent $\overline{MW}$ would have resulted. However, the assumed C_T range was the same as that used here in actual VPO measurements with 1,2-dichloroethane solvent. Furthermore, if only the carboxylic acid contribution to C_T for Cerro Negro acids had been considered, lower estimates for apparent $\overline{MW}$ would have been obtained. Nevertheless, even though the calculated apparent $\overline{MW}$ carry implicit assumptions which would affect the magnitude of estimated errors in VPO $\overline{MW}$ by as much as a factor of 2, this semiquantitative IR analysis of hydrogen-bonding interactions clearly demonstrates the following conclusions: 1) Solute-solute association induced by hydrogen-bonding cannot even account for errors observed in VPO-determined $\overline{MW}$ for distillable acids, much less the much greater errors encountered for $>700^\circ\text{C}$ acid fractions. 2) The absolute effect of hydrogen-bonding between carboxylic acids on apparent $\overline{MW}$ is nearly independent of $\overline{MW}$. The relative error actually

decreases. This trend is totally inconsistent with the observed decrease in accuracy for VPO $\overline{MW}$ with increasing AEBP/ $\overline{MW}$. 3) Thus, errors observed in VPO $\overline{MW}$ for acids arise from other types of interactions, e.g., charge-transfer between aromatic systems or other types not directly revealed by IR bands considered here. For example, the minimal effect of quinoline on the carboxyl bands of *p*-toluic acid in figure 21 does not preclude a significant degree of association through other types of interaction; it simply indicates little direct involvement of the carbonyl group in hydrogen-bonding interactions. 4) Finally, the best approach toward compensating for hydrogen-bonding or other intermolecular associations in VPO is clearly to conduct the measurements on the most dilute solutions possible. Given their quadratic (or higher) dependence on C_T and generally unknown equilibrium constants, no general method for correcting VPO data obtained at high concentrations can be derived. Similarly, apparent linearity of VPO data versus C_T does not prove the absence of these effects nor imply accuracy in the extrapolated $\overline{MW}$.

TABLE 6 - Carboxylic acid molar absorptivities (ϵ_M), dimerization constants (K_D), and the effect of dimerization on apparent $\overline{MW}$ measured by VPO

Compound/Fraction	ϵ_M (Lm ⁻¹ mm ⁻¹)	K_D (Lm ⁻¹ , 1,2-dichloroethane)	$\overline{MW}$ (g/m)			$\Delta \overline{MW}$ (g/m)	
			"Best Available" ³	Actual VPO ⁴	Apparent VPO ⁵	Absolute	Relative %
n-Decanoic acid	61.2	147	172.27	-	194	22	13
Cyclopentanecarboxylic acid	55.4	134	114.14	-	133	19	14
p-Toluic acid	32.4	179	136.15	-	160	24	18
Cerro Negro							
200-425°C ¹	46.8	122 ²	295	295	315	20	7
425-550°C ¹	53.2	122 ²	377	442	397	20	5
550-700°C ¹	46.2	122 ²	470	542	489	19	4

¹ Subfraction 5. Yields (wt pct total acids) were 62, 57, and 36 for 200-425°, 425-550° and 550-700° C, respectively.

² Average for all boiling ranges.

³ After table 5.

⁴ After table 4, 1,2-dichloroethane solvent.

⁵ Calculated from K_D and best available $\overline{MW}$ assuming VPO measurements were obtained at $C_T = 0.3, 0.6$, and 1.5 g/L in all cases.

⁶ Error between best available and predicted VPO $\overline{MW}$.

FIGURE 24. - Concentration dependence of $1/\overline{MW}$, the reciprocal of the weighted average MW for monomeric and dimeric species, calculated from data in table 6 using equations 13 and 16 (see text).

SUMMARY AND CONCLUSIONS, PART B

The average molecular weight $\overline{MW}$ of Cerro Negro crude (638) is clearly greater than that of conventional crudes, but only by a factor of 2 or 3. Cerro Negro resid has a $\overline{MW}$ comparable to that of other crudes; thus, the higher $\overline{MW}$ for the crude simply results from its lower distillate content.

Results for $\overline{MW}$ of the crude were obtained by fractionation and determination of $\overline{MW}$ on each fraction by one or more techniques: vapor pressure osmometry (VPO), nonaqueous titration (NAT), and gas chromatography (GC). These results were also used to evaluate the applicability and limitations of each technique. VPO was suitable only for mid-distillates and neutral or saturated hydrocarbon fractions from heavy distillates and residues. VPO generally gave erroneously high results for acid and base fractions because of 1) intersolute association and 2) solute-solvent association. The latter phenomenon was especially severe when pyridine was used as the solvent. NAT was the best of the available techniques for acid or base fractions. Gas chromatographic $\overline{MW}$ for saturate fractions were in good agreement with those obtained by VPO. Overall, accuracy of $\overline{MW}$ calculated from measurements on fractions was much higher than obtained directly on whole crudes or similar gross mixtures.

It should be noted that the effects of solute-solvent and solute-solute association noted here for VPO apply to other techniques as well. For example, the previously mentioned association of THF with phenols has been used to effect their separation as a class in SEC (61,62). Also, dimerization of carboxylic acids in dichloromethane has similarly been exploited for their isolation from petroleum (77). Prior work indicates that interaction of THF (43) and pyridine (76) with phenols and other types of polar solutes causes their MW versus SEC elution time correlation to differ significantly from those of polystyrenes and other commonly employed SEC calibration standards. However, other examples of association noted here, such as that between neutral-aromatics, are not as widely recognized. In general, if the solute-solute or solute-solvent association effects for the materials used to construct the SEC (or VPO) MW calibration curve do not closely resemble those of the samples, significant errors in the resulting SEC (or VPO) $\overline{MW}$ will occur. Many researchers using SEC have indicated general awareness of association-related inaccuracy in determination of $\overline{MW}$, but often these effects

are dismissed with explanations like "only comparative MW distributions were desired." However, in cases where "bimodal MW distributions" are reported, for example, the true MW distribution could be Gaussian and the bimodal appearance may simply reflect highly associated versus unassociated species. This type of gross misinterpretation could even affect the final conclusions from the work. An extreme case of the above was recently reported by Nguyen and Filby (78), who added pure low molecular weight metal-containing compounds to petroleum residue fractions and found that the spiked compound appeared to span the entire observed MW range, because of its association with the petroleum compounds. Given that level of association, no valid conclusions concerning $\overline{MW}$ distributions of metal-containing compounds, such as those obtained with SEC-inductively coupled plasma hyphenated instrumentation, are possible without both careful control of the experimental conditions and accounting of the effects of association on experimental data.

The general inapplicability of conventional VPO theory and practice to determination of $\overline{MW}$ of gross fractions such as whole petroleum residues, asphaltenes, and the like was demonstrated. Traditional theory, which was developed for synthetic polymers, does not contain provisions for discrete chemical interactions such as those discussed here. Furthermore, as pointed out in related work on coal-derived materials (79), fossil matter cannot generally be viewed as a series of "polymer homologs," which forms the basis of conventional VPO theory. Saturate fractions come closest to the ideal polymer homologs model, which along with their minimal tendency for association explains why they yielded the best VPO data of all fractions examined.

The available evidence supports charge-transfer or an analogous type of bonding between aromatic systems as the dominant intermolecular association mechanism rather than hydrogen-bonding or other direct functional group pairing. Thus, heteroatoms and metals increase association indirectly by enhancing charge-transfer between aromatic moieties rather than through direct coupling. Also, significant association between neutral aromatic compounds occurred, especially in the absence of saturated hydrocarbons.

The presence of significant quantities of distinct macromolecules with MW of several thousand in heavy petroleum is an improbable concept which largely originated from erroneous $\overline{MW}$ estimates obtained under conditions promoting

intermolecular association. Similarly, commonly observed phenomena such as asphaltene precipitation, abnormally high viscosities or specific gravities for certain oils, and the presence of apparently distillable materials in nondistillable fractions noted in section A of this report all reflect effects of intermolecular association rather than the presence of large macromolecules. However, in a phenomenological sense, these associates could be considered to be macromolecules because they behave as such.

Some of the most interesting results obtained indicated a "dispersive" action or capability for negating association within a given compound class or type by another class. For example, the presence of saturates, e.g., in whole neutral fractions, resulted in less apparent association between 550-700° C and >700° C neutral-aromatic compounds*. Also, 1:1 mixtures of acids and bases yielded lower apparent MW than either fraction by itself in two cases. However, these anomalous results cannot generally be explained nor absolutely assured to be outside the range of experimental error. Nevertheless, such effects correlate with equally mysterious solubility behavior observed elsewhere in this work and in the literature. For example, it is widely recognized that asphaltene yields vary significantly with the solvent used for their precipitation. Moreover, material precipitated in pentane, for example, cannot be redissolved in heptane to the extent predicted by their difference in asphaltene yields. Similarly, whole >700° C Cerro Negro residue can be dissolved in cyclohexane, but >700° C acid and base fractions are only partially soluble. These effects are consistent with the ability of some heavy oil components to prevent association and subsequent precipitation of others. Obviously, the details of these effects remain to be worked out.

However, the economic potential for the technical capability to manipulate association effects is quite large. For example, minimizing association would increase field production and decrease pipeline cost by lowering viscosity. Potentially, catalyst pore size and other refining parameters could also be optimized if the degree of association, i.e., effective molecular size, could be controlled. In addition, the results

*Conceivably, this effect could occur in a manner analogous to clathrate formation between saturates and aromatics in solid phases, which is well documented.

obtained in section A indicate that higher distillate yields could even be obtained by minimizing molecular association. Finally, better asphalts may result from blending to maximize association effects. Long term research toward a better understanding of association effects can be justified by any of the above potential practical gains, or simply from the viewpoint of improving heavy oil analysis methods.

REFERENCES

1. Smith, N. A. C., H. M. Smith, O. C. Blade, and E. L. Garton. The Bureau of Mines Routine Method for the Analysis of Crude Petroleum. BuMines Bull. No. 490, 1951, 82 pp.
2. Coleman, H. J., J. E. Dooley, D. E. Hirsch, and C. J. Thompson. Anal. Chem., v. 45, 1973, p. 1724.
3. Ali, M. F., M. U. Hasan, A. M. Bukhari, and M. Saleem. Hydrocarbon Processing, v. 64, No. 2, 1985, p. 83.
4. Domansky, C. J. AOSTRA J. Res., v. 2, 1986, p. 191.
5. Boduszynski, M. M. Energy Fuels, v. 1, 1987, p. 2.
6. Shay, J. Y., and P. W. Woodward. Amer. Lab., v. 18, Issue 10, 1986, p. 114.
7. American Society for Testing and Materials. Section 5 - Petroleum Products, Lubricants, and Fossil Fuels. Philadelphia, PA, 1983, v. 04.08 and 05.01-05.05.
8. Annual Book of ASTM Standards, Section 5, "Petroleum Products, Lubricants, and Fossil Fuels," Volume 05.01, "Petroleum Products and Lubricants," (1):D 56-D 1660, 1985. Note: This proposed method is not published in later editions of the Annual Book of ASTM Standards.
9. Worman, J. C., and L. E. Green. Anal. Chem., v. 37, 1965, p. 1620.
10. Petroff, N., A. Hoscheitt, and J. P. Durand. J. Chromatogr., v. 395, 1987, p. 241.
11. Green, J. B., P. L. Grizzle, J. S. Thomson, J. Y. Shay, B. H. Diehl, K. W. Hornung, and V. Sanchez. Analysis of Heavy Oils: Method Development and Application to Cerro Negro Heavy Petroleum. Distillation and Determination of Routine Chemical/Physical Properties. Topical Report NIPER-160, February 1988, 127 pp.
12. DiSanzo, F. P., C. J. Lowther, R. E. Yoder, and J. L. Lane. J. Chromatogr. Sci., v. 26, 1988, p. 39.

13. Anonymous. "BPO Crude Oil Analysis Data Bank Users Guide," U.S. Department of Energy Report DOE/BC-87/5/SP, Bartlesville, OK, 1987, 36 pp.
14. Drushel, H. V. *Anal. Chem.*, v. 49, 1977, p. 932.
15. Universal Oil Products Co. UOP Laboratory Test Methods for Petroleum and Its Products. Des Plaines, IL, 1985, v. I and II.
16. Drushel, H. V. *Amer. Chem. Soc., Div. Petrol. Chem. Prepr.*, v. 14, 1969, p. B232.
17. Lubkowitz, J. A., H. O. Buenafama, and V. A. Ferrari. *Anal. Chem.*, v. 52, 1980, p. 233.
18. Demaison, G. J. *Bull. Am. Assoc. Petrol. Geol.*, v. 61, 1977, p. 1950.
19. Butler, R. D. *Chromatography in Petroleum Analysis*, edited by K. H. Altgelt and T. H. Gouw. M. Dekker, New York, NY, 1979, pp. 75-89.
20. Weast, R. C. (Editor). *Handbook of Chemistry and Physics*, 50th Edition. CRC Press, Cleveland, OH, 1969.
21. Glinzer, O. *Erdol und Kohle-Erdgas-Petrochemie-Brennstoff Chemie*, v. 38, No. 5, 1985, p. 213.
22. Arnold, V. E. *Oil and Gas Journal*, v. 82, No. 3, 1984, p. 103.
23. Trestianu, S., G. Sironi, C. Saravalle, F. Munari, M. Galli, G. Gaspar, J. M. Colin, and J. L. Jovelin. *J. High Resolut. Chromatogr. Chromatogr. Commun.*, v. 8, 1985, p. 771.
24. Lipsky, S. R., and M. L. Duffy. *J. High Resolut. Chromatogr. Chromatogr. Commun.*, v. 9, 1986, p. 376.
25. Schwartz, H. E., J. W. Higgins, and R. G. Brownlee. *LC-GC*, v. 4, 1986, p. 639.
26. Schwartz, H. E., R. G. Brownlee, M. M. Boduszynski, and F. Su. *Anal. Chem.*, v. 59, 1987, p. 1393.
27. Mondragon, F., and K. Ouchi. *Fuel*, v. 63, 1984, p. 61.
28. Southern, T. G., A. Iacchelli, D. Cuthieil, and M. L. Selucky. *Anal. Chem.*, v. 57, 1985, p. 303.
29. Unpublished results from an ongoing NIPER study, "Determination of the Composition and Chemistry of Heavy Crudes, Intermediate Process Streams, Products, and By-products."
30. Bunger, J. W., K. P. Thomas, and S. M. Dorrence. *Fuel*, v. 58, 1979, p. 183.

31. Spencer, W. A., J. F. Galobardes, M. A. Curtis, and L. B. Rogers. Separation Sci. Technol., v. 17, 1982, p. 797.
32. Aalund, L. Oil and Gas Journal, v. 74, No. 15, 1976, p. 78.
33. NIPER-DOE Crude Oil Data Bank, Sample No. 59190.
34. McKay, J. F., S.-L. Chong, and G. W. Gardner. Liquid Fuels Technol., v. 1, 1983, p. 259.
35. Boduszynski, M. M. American Chemical Society, Div. Fuel Chem. Prepr., v. 30, No. 3, 1985, p. 365.
36. Young, L.-J. S., T. Hara, and N. C. Li. Fuel, v. 63, 1984, p. 816.
37. McKay, J. F., and S.-L. Chong. Liquid Fuels Technol., v. 1, 1983, p. 289.
38. Champagne, P. J., E. Manolakis, and M. Ternan. Fuel, v. 63, 1984, p. 423.
39. Sanchez, V., E. Murgia, and J. A. Lubkowitz. Fuel, v. 63, 1984, p. 612.
40. Guieze, P., and J. M. Williams. J. Chromatogr., v. 312, 1984, p. 261.
41. Hall, G., and S. P. Herron. American Chemical Society, Div. Petrol. Chem. Prepr., v. 24, 1979, p. 924.
42. Irani, C. A., D. S. Schuster, and R. T. Yin. American Chemical Society, Div. Fuel Chem. Prepr., v. 30, No. 1, 1985, p. 158.
43. Evans, N., T. M. Haley, M. J. Mulligan, and K. M. Thomas. Fuel, v. 65, 1986, p. 694.
44. Drake, J. A. G., and D. W. Jones. Fuel, v. 62, 1983, p. 835.
45. McKay, J. F., P. M. Harnsberger, R. B. Erikson, T. E. Cogswell, and D. R. Latham. Fuel, v. 60, 1981, p. 17.
46. McKay, J. F., D. R. Latham, and W. E. Haines. Fuel, v. 60, 1981, p. 27.
47. Aczel, T., J. A. Laramee, and G. J. Hansen. Proc. 30th Am. Conf. Mass. Spectrom. Allied Topics, 1982, p. 808.
48. Rechsteiner, C. E., T. H. Attoe, and M. M. Boduszynski. Proc. 33rd Am. Conf. Mass Spectrom. Allied Topics, 1985, p. 937.
49. Boduszynski, M. M., R. J. Hurtubise, and H. F. Silver. Fuel, v. 63, 1984, p. 93.
50. Steuer, W., K. Jost, and I. Halasz. Chromatographia, v. 20, 1985, p. 13.

51. Jost, K., W. Steuer, and I. Halasz. *Chromatographia*, v. 20, 1985, p. 700.
52. Acevedo, S., B. Mendez, A. Rojas, I. Layrisse, and H. Rivas. *Fuel*, v. 64, 1985, p. 1741.
53. El-Mohamed, S., M.-F. Achard, F. Hardouin, and H. Gasparoux. *Fuel*, v. 65, 1986, p. 1501.
54. Cassani, F., and G. Eglinton. *Chem. Geol.*, v. 56, 1986, p. 167.
55. Acevedo, S., O. Leon, H. Rivas, H. Marquez, G. Escobar, and L. Gutierrez. *Amer. Chem. Soc., Div. Petrol. Chem. Prepr.*, v. 32, 1987, p. 426.
56. Moschopedis, S. E., J. F. Fryer, and J. G. Speight. *Fuel*, v. 55, 1976, p. 227.
57. Al-Jarrah, M. M. F., and R. L. Apikian. *J. Chem. Technol. Biotechnol.*, v. 39, 1987, p. 231.
58. Leon, V. *Fuel*, v. 66, 1987, p. 1445.
59. Schanne, L., and M. W. Haenel. *Fuel*, v. 60, 1981, p. 556.
60. Krigsbaum, W. R., and R.-J. Roe, "Measurement of Osmotic Pressure," in *Treatise on Analytical Chemistry, Part 1*, v. 7, edited by I. M. Kolthoff and P. J. Elving, Wiley-Interscience, NY, 1967, p. 4461.
61. Philip, C. V., and R. G. Anthony. *Amer. Chem. Soc., Div. Fuel Chem. Prepr.*, v. 24, No. 3, 1979, p. 204.
62. Philip, C. V., and R. G. Anthony. *Fuel*, v. 61, 1982, p. 357.
63. *Instruction Manual for Model 232A Molecular Weight Apparatus*, Wescam Instrument Co., Santa Clara, CA.
64. Cross, A. O., and R. A. Jones. *Practical Infrared Spectroscopy*. Butterworths LTD, London, 3rd. Ed., 1969, p. 43-44.
65. Silverstein, R. M., G. C. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds*. J. Wiley, NY, 4th Ed., 1981, Chapter 3.
66. *IR SCOT-Infrared Structural Correlation Tables and Data Cards*. Heyden and Son LTD, London, 1968, Table 4.
67. Green, J. B., B. K. Stierwalt, J. A. Green, and P. L. Grizzle. *Fuel*, v. 64, 1985, p. 1571.

68. Sturm, G. P., Jr., S. Y. Tang, R. D. Grigsby, D. H. Hirsch, and C. A. Treese. The Application of Mass Spectrometric Methods in the Characterization of the 200-425° C and 425-550° C Acid, Base, and Neutral Fractions of Cerro Negro Crude. NIPER Topical Report No. 111, 1985, 46 pp.
69. Rossini, F. D., K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel. API Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, Carnegie Press, Pittsburgh, PA, 1953.
70. Speight, J. G., Amer. Chem. Soc., Div. Petrol., Chem. Prepr., v. 31, 1986, p. 818.
71. Boduszynski, M. M. Chemistry of Asphaltenes, J. W. Bunger, and N. C. Li (Editors), Amer. Chem. Soc., Washington, DC, 1981, Chapter. 7.
72. Yen, T. F. Amer. Chem. Soc., Div. Fuel Chem. Prepr., v. 15, No. 1, 1971, p. 93.
73. Quinga, E. M., and J. W. Larsen. Energy and Fuels, v. 1, 1987, p. 300.
74. Petelenz, B. U., and H. F. Schurvell. Can. J. Chem., v. 58, 1980, p. 353.
75. Robbins, G. A., R. A. Winschel, and F. P. Burke. Amer. Chem. Soc., Div. Fuel Chem. Prepr., v. 30, No. 4, 1985, p. 155.
76. Buchanan, D. H., L. C. Warfel, S. Bailey, and D. Lucas. Energy Fuels, v. 2, 1988, p. 32.
77. Cogswell, T. E., J. F. McKay, and D. R. Latham. Anal. Chem., v. 43, 1971, p. 1766.
78. Nguyen, S. N., and R. H. Filby. Metal Complexes in Fossil Fuels, R. H. Filby and J. F. Branthaver (Editors), Amer. Chem. Soc., Washington, DC, 1987, p. 384.
79. Collins, C. J., R. Triolo, and M. H. Lietzke. Fuel, v. 63, 1984, p. 1202.

**ANALYSIS OF HEAVY OILS: METHOD DEVELOPMENT AND APPLICATION
TO CERRO NEGRO HEAVY PETROLEUM**

**Preliminary Separation and Analysis of Acid, Base, Saturate,
and Neutral-Aromatic Fractions**

Topical Report

**By
J.B. Green
G.P. Sturm, Jr.
J.W. Reynolds
J.S. Thomson
S. K.-T. Yu
R.D. Grigsby
S.-Y. Tang
J.Y. Shay
D.E. Hirsch
V. Sanchez**

October 1988

Work Performed Under Contract No. FC22-83FE60149

**Prepared for
U.S. Department of Energy
Assistant Secretary for Fossil Energy**

**W.D. Peters, Project Manager
Bartlesville Project Office
P.O. Box 1398
Bartlesville, OK 74005**

**Prepared by
IIT Research Institute
National Institute for Petroleum and Energy Research
P.O. Box 2128
Bartlesville, OK 74005**

**DO NOT MICROFILM
THIS PAGE**

(This page intentionally left blank.)

TABLE OF CONTENTS

	<u>Page</u>
Foreword.....	iii
Abstract.....	x
Acknowledgment.....	xi
Introduction.....	1
Evaluation of Available Separation Approaches and Methodology.....	3
Basic Considerations.....	3
Methods Based on Precipitation or Solubility Effects.....	6
Solvent Extraction Methods.....	6
LC Methods.....	9
Single Column Methods.....	9
Multidimensional Methods.....	14
Summary of Nonaqueous Ion Exchange LC Separation Development.....	22
Separation of Neutrals into Saturates and Neutral-Aromatics.....	30
Conclusions from the Literature Evaluation and Preliminary Work.....	31
Experimental.....	33
Apparatus.....	33
Materials.....	34
Methods.....	35
ABN Separations.....	35
Saturate-Aromatic Separations.....	38
Mass Spectrometric Analysis of 200-425° C and 425-550° C Acid, Base, Saturate, and Aromatic Concentrates.....	39
Other Analyses.....	40
Results and Discussions.....	40
Mass and Elemental Balances.....	41
Further Analysis of Saturate Fractions.....	52
Distribution of Nitrogen-Containing Compounds.....	59
Distribution of Oxygen-Containing Compounds.....	82
Distributions of Hydrocarbons and Sulfur-Containing Compounds.....	99
Concluding Remarks.....	104
References.....	106
Appendix 1 - Current Procedures for the Preparation of Resins Used in the NIPER Nonaqueous Ion Exchange Chromatographic Procedure.....	115
Appendix 2 - Comprehensive Listing of Results From Individual ABN and Saturate/Neutral-Aromatic Separations.....	119
Appendix 3 - Relative Resistance of Neutral Nitrogen Compounds to Hydrodenitrogenation.....	127

TABLES AND ILLUSTRATIONS

<u>Table</u>	<u>Page</u>
1 Comparative acid-base-neutral yields from extraction versus nonaqueous ion exchange chromatography.....	8
2 Isomeric classes in petroleum.....	10
3 Results from evaluation of SESC.....	12
4 Summary of selected multidimensional separation schemes.....	16

TABLES AND ILLUSTRATIONS (cont'd)

<u>Table</u>	<u>Page</u>
5 ABN separation yields (wt %) from Wilmington, CA, 370-535° C distillate obtained using different ion exchange resins and preparation.....	23
6 Resin artifact yields (mg) from blank determinations on resins in table 5.....	25
7 Mass balances of separations.....	42
8 Elemental analysis of selected ABN fractions.....	43
9 Distribution of nitrogen compounds in ABN and neutral-aromatic fractions.....	46
10 Distribution of sulfur compounds in ABN and neutral-aromatic fractions.....	47
11 Distribution of oxygen compounds in ABN and neutral-aromatic fractions.....	49
12 Analysis of the Cerro Negro saturates by ASTM method D 2786.....	57
13 Monoaromatic contamination of saturates as determined by UV absorbance at 254 nm.....	58
14 IR characteristics of selected compounds exhibiting N-H stretching bands.....	60
15 Concentrations of N-H compounds in selected fractions determined by IR.....	62
16 Results from nonaqueous titration with perchloric acid.....	73
17 Composition of Cerro Negro 200-425° C and 425-550° C base concentrates (wt %) from mass spectrometric analysis.....	78
18 Results for compound class distributions in acid fractions determined by different methods.....	91
19 Composition of Cerro Negro 200-425° C and 425-550° C acid concentrates (wt. %) from mass spectrometric analysis.....	92
20 Composition of the Cerro Negro 200-425° C and 425-550° C neutral-aromatic concentrates (wt %) from mass spectrometric analysis.....	101
21 Mass balances from sulfide separations.....	103
A2-1 Conditions for ABN separations.....	121
A2-2 Results of ABN separations.....	122
A2-3 ABN results on Cerro Negro fractions determined with the current (8/88) versions of the method.....	123
A2-4 Results of saturate-aromatic separations.....	124
A3-1 Nitrogen distribution in Wilmington gas oil and hydrotreated products.....	128
A3-2 Nitrogen distribution in Mayan gas oil and hydrotreated products.....	129

<u>Figure</u>	<u>Page</u>
1 HPLC chromatograms showing the effect of the order of anion versus cation resins on the partitioning of pyrrolic benzologs (shaded region) in Wilmington 370-535° C distillate into acid versus base fractions.....	28
2 HPLC analysis of strong and weak acid concentrates from SRC-II >325° C residue.....	29
3 Scheme for ABN separation of distillates.....	36
4 Scheme for ABN separation of the residue.....	37

TABLES AND ILLUSTRATIONS (cont'd)

Figure	Page
5 DNAP separation of 0.1 g 200-425° C neutrals, using forward elution for monoaromatics + saturates and diaromatics, and backflush mode for elution of >2-ring aromatics.....	53
6 Isocratic separation of n-heptadecane and toluene on silica. n-Pentane solvent, 20 mL/min.....	54
7 (A) Initial separation of saturates + monoaromatics from ≥2-ring compounds from 425-550° C neutrals on DNAP. (B) Reseparation of first fraction in (A) on silica to obtain saturates and mono-aromatics.....	55
8 Infrared spectra of 425-550° C ABN fractions and whole distillate. Concentrations (mg/mL) in 1,2-dichloroethane were: whole distillate - 107, acids - 19.1, bases - 23.7, and neutrals - 102.....	61
9 Infrared spectra of high boiling neutrals versus the corresponding whole distillate/residue.....	63
10 Z-series distributions of nitrogen ($C_nH_{2n+Z}N$) compounds in 200-425° C acid, base, and neutral-aromatic concentrates.....	65
11 Z-series distributions of nitrogen ($C_nH_{2n+Z}N$) compounds in 425-550° C acid, base, and neutral-aromatic concentrates.....	66
12 Illustration of the Z-series concept. (A) Z = -5 for all alkylpyridines regardless of carbon number or number of substituents. (B) Examples of the wide variation in structure possible for a given empirical formula: $C_{18}N_{21}N$ (Z = -15). (C) Z-values of representative pyrrolic benzologs. See text.....	68
13 Carbon number distribution for $C_nH_{2n-15}N$ compounds in 200-425° C acid, base, and neutral-aromatic concentrates.....	70
14 Carbon number distribution for $C_nH_{2n-21}N$ compounds in 425-550° C acid, base, and neutral-aromatic concentrates.....	71
15 Z-series distributions of nitrogen (N), nitrogen-sulfur (NS) and nitrogen-oxygen (NO) compounds in 200-425° C bases.....	76
16 Z-series distributions of nitrogen (N), nitrogen-sulfur (NS) and nitrogen-oxygen (NO) compounds in 425-550° C bases.....	77
17 IR spectra of plain versus derivatized 200-425° C acid.....	85
18 IR spectra of plain versus acylated >700° C strong acids.....	86
19 Titration curves of benzoic acid plus 1,2,3,4-tetrahydro-carbazole (A) and Cerro Negro 200-425° C whole acids (B).....	87
20 ^{119}Sn NMR spectrum of bis-(tri-n-butyltin) oxide (TBTO) derivatized 425-550° C acids. imp = impurity in the TBTO reagent. SB = side band of TBTO produced from coupling of ^{119}Sn with ^{13}C in n-butyl substituent.....	89
21 Z-series distribution of oxygen ($C_nH_{2n+Z}O$) compounds in 200-425° C acid, base, and neutral-aromatic concentrates.....	95
22 Z-series distribution of oxygen ($C_nH_{2n+Z}O$) compounds in 425-550° C acid, base, and neutral-aromatic concentrates.....	96
23 Z-series distributions of hydrocarbons (H), sulfur compounds (S), and disulfur compounds (S_2) in 200-425° C neutral-aromatics concentrate.....	99
24 Z-series distributions of hydrocarbons (H), sulfur compounds (S), and disulfur compounds (S_2) in 425-550° C neutral-aromatics concentrate.....	100

ABSTRACT

Cerro Negro 200–425°, 425–550°, and 550–700° C distillates and >700° C residue were separated into acid, base, and neutral concentrates using an improved nonaqueous ion exchange liquid chromatographic procedure. Neutral concentrates were further separated into neutral-aromatic and saturated hydrocarbon fractions. A dual column, normal phase high performance liquid chromatographic method was developed for the saturate-aromatic separation. Mass and elemental balances are given for separations of all distillates and the residue. In addition, fractions from the 200–425° C and 425–550° C distillates were analyzed by high resolution mass spectrometry.

The applicability of published separation approaches and methods to heavy oil analysis is critically reviewed; the bulk of the available methodology developed for conventional petroleum and synfuels was found to be unproven or unsuitable for heavy oil analysis. The separation scheme developed for Cerro Negro is designed to overcome deficiencies and resolve ambiguities identified in prior methods. However, its overall effectiveness is heavily reliant on the success of the initial acid-base-neutral (ABN) separation step. Thus, the results obtained are discussed in the context of evaluating the effectiveness of the ABN separation method itself, and determining its impact on results from subsequent separations and analyses, as well as reporting on the composition of the crude per se. Finally, the need for further separation of the ABN concentrates to obtain definitive analysis of specific compound classes is addressed.

Cerro Negro was found to contain 18.2 weight percent acids, 17.6 weight percent bases, 46.9 weight percent neutral aromatics, and 14.7 weight percent saturated hydrocarbons. Saturate fractions contained predominantly cycloparaffins, neutral-aromatics were largely comprised of aromatic hydrocarbons and sulfur compounds, bases were largely nitrogen-containing compounds, and acids were mostly oxygen-containing compounds and nitrogen compounds of pyrrolic type.

ACKNOWLEDGMENT

The financial support of the U. S. Department of Energy is gratefully acknowledged. Also, the technical contributions of Drs. S. E. Scheppele, P. L. Grizzle, and J. C. Brown are recognized. In addition, the authors thank Drs. M. M. Boduszynski, P. L. Grizzle, and S. E. Scheppele for reviewing the initial draft, and W. D. Good, W. D. Peters, P. R. Stapp, and R. P. Anderson for their review of the revised copy. Finally, special thanks are extended to Ms. Joan Haimson and the NIPER drafting department for manuscript typing and preparation.

**DO NOT MICROFILM
THIS PAGE**

(This page intentionally left blank.)

PRELIMINARY SEPARATION AND ANALYSIS OF ACID, BASE, SATURATE, AND NEUTRAL-AROMATIC FRACTIONS

by

J. B. Green, G. P. Sturm, Jr., J. W. Reynolds,
J. S. Thomson, S. K.-T. Yu, R. D. Grigsby, S.-Y. Tang,
J. Y. Shay, D. E. Hirsch, and V. Sanchez

INTRODUCTION

The initial step toward separation and analysis of Cerro Negro heavy oil was distillation, described in Chapter 1. General chemical/physical properties of the distillates/residue obtained with more or less conventional methodology also appear in Chapter 1. This chapter initiates discussion of the second phase of the work, chemical separation of the distillates/residue into compound classes. Specifically, Chapter 2 addresses preliminary separation of each distillate/residue into acidic, basic, and neutral concentrates, and subdivision of the whole neutrals into saturated hydrocarbon and neutral-aromatic fractions.

The initial chemical separation step has a major impact on the ultimate success of the analysis. For example, incomplete partitioning of a given compound class into a given fraction typically causes results for that class to be low, and remnants of the class carrying over to other fractions may interfere in the analysis of other classes. The basic function of the initial separation is to generate fractions containing generic types suitable for more detailed separations, if desired. The most important objectives for chemical separations in general are: 1) to separate interfering compound classes, 2) to concentrate minor classes which, although present in low abundance, potentially have a major impact on properties and processing behavior, and 3) to yield quantitative (weight percent) distributions of compound classes or types present. Practical constraints must also be considered. Generally, the separation process should 1) introduce a minimum of impurities, 2) yield essentially 100% recovery and acceptable precision, and 3) cause minimal alteration of the sample. For this project in particular, separations must be applicable to non-distillable fractions, since the residue accounts for nearly half of the whole crude. Furthermore, for comparison of crude composition as a function of boiling range, identical or at least equivalent methodology must be applied to all distillates and the residue. Otherwise, i.e., if different

methods are used for various boiling ranges, yields of a given class, e.g., basic nitrogen compounds, are typically not directly comparable. Thus, the initial objective of work for this chapter was simply to prepare fractions consistent with the three general objectives stated above. Later, its scope broadened to include development of an appropriate separation method, its application to Cerro Negro, and analysis of the resulting fractions for the purpose of both verification of the separation method and determination of the composition of the crude.

It is difficult to estimate the number of papers published on the subject of compound class separations of fuels, crudes, and petroleum/synfuel-related products; but it certainly ranges into the thousands. Given this magnitude of available information, the authors initially assumed that the major task at hand would be selecting one of many potential methods for work on Cerro Negro. On the contrary, virtually all published methods or approaches were summarily dismissed because the available data showed that they failed to meet the three objectives listed above and/or suffered unduly from practical constraints. In other cases, there was insufficient data to determine whether a method was suitable. In the latter situation, if the method appeared promising it was evaluated experimentally.

For the benefit of the reader faced with performing a similar evaluation, or one simply interested in the details of prior work in compound class separations, a summary of the literature evaluation is given below. While reading this section, it should be recognized that methods and approaches were surveyed for direct relevance to this work and their specific ability to meet the stated objectives. Thus, the conclusion that a given method was generally unsuited, insufficiently verified, precise, or otherwise inappropriate for work on Cerro Negro should not be construed as an attempt to belittle the work or to discredit conclusions drawn from its application toward other objectives.

Finally, although the initial survey of methods was conducted in 1980-1981, the following sections have been updated to maximize their benefit to the reader. Since much of the subsequent work in class separations has dealt with evaluation, refinement, and/or application of earlier methods rather than development of new methods or approaches, the more recent papers cited typically provide further information on a method that was considered, rather than a new method developed in the interim. To avoid confusion, methodology

developed concurrently or after completion of the Cerro Negro separations, i.e., too late for consideration in the evaluation, is identified as such.

Evaluation of Available Separation Approaches and Methodology

Basic Considerations

Fundamental aspects of the various separation approaches such as their relative efficiency, general selectivity, flexibility, and overall speed may be used to screen potential methods. Similarly, practical limitations eliminate many approaches from consideration. For example, methods requiring dissolution in aqueous phases are not practical because of the inherent insolubility of heavy oils in water; similarly, methods requiring volatilization are not practical for the distillation residue, and potentially even for higher boiling distillates.

Solvent extraction procedures have been used to separate compound classes in fuels; e.g., extraction of acids with basic solutions. The distribution of a given solute or class may be described by its partition coefficient (K_p)(1),

$$K_p = \frac{[x]_{\text{raff.}}}{[x]_{\text{extr.}}}, \quad (1)$$

where x is the solute and the two immiscible phases are arbitrarily designated raffinate and extract. Since $[x] = (W_x)/(MW_x)(V)$ -- where W is weight, MW is molecular weight, and V is volume -- K_p may also be written:

$$K_p = \frac{(W_x)_{\text{raff.}}}{(W_x)_{\text{extr.}}} \cdot \frac{V_{\text{extr.}}}{V_{\text{raff.}}} \quad (2)$$

K_p varies with the nature of the solute or class of solutes, solvents used, and environmental factors such as temperature. Selectivity in solvent extraction may be controlled by varying solvents, adding solvent modifiers such as ion pairing agents, and changing environmental factors. Since each extraction performed corresponds to one theoretical plate, the practical efficiency achievable with ordinary separatory funnels and related glassware in a reasonable time is quite low. However, modern opposing flow-type extractors, also referred to as countercurrent chromatographs, can achieve efficiencies ranging from 100 to 1,000 theoretical plates, although usually on relatively small quantities of material.

Precipitation or solubility phenomena have also been employed for compound class separations, e.g., HCl precipitation of bases as salts, and precipitation of asphaltenes with n-alkane solvents. Theoretically, the effectiveness of the separation is governed solely by the relative solubilities of the targeted class versus others present. Frequently, however, coprecipitation, adsorption, and other nonideal effects determine actual separation quality.

By far, liquid chromatography (LC) has received the most widespread attention for class separations of fuels. This technique has far wider flexibility, higher theoretical efficiency, and significant practical advantages over other methods. Liquid-liquid chromatography is analogous to solvent extraction, both theoretically and in terms of selectivities achievable. However, liquid-solid chromatography is traditionally preferred for compound class separations, because relative retention of solutes on adsorbents is primarily determined by the types and orientation of functional groups present (2). Although a detailed discussion of LC theory and applications is well beyond the scope of this report, selected aspects pertaining to this evaluation are mentioned below.

Because of its long-standing reliance on and, in many cases, pioneering work in LC compound class methods, the petroleum industry recognizes and still actively employs many classical LC methods, a number of which have been standardized by organizations such as ASTM. Nevertheless, the advantages of modern, high performance LC (HPLC) were widely known even in 1980 (e.g., see ref. 3), when work on Cerro Negro began. For example, HPLC columns typically generate 100 times as many theoretical plates per unit length as classical, gravity flow columns. Furthermore, HPLC flow rate and solvent composition is precisely controlled and programmable. Also, a variety of HPLC detectors are available for continual monitoring of the separations progress, whereas classical separations are typically performed "on the blind." Finally, since HPLC columns are used repeatedly, their retention characteristics can be carefully calibrated with standard compounds and/or samples prior to use; classical columns cannot be individually calibrated since they are only used once. Thus, one criterion used in the evaluation of some of the older methods was the ease in adapting or modernizing them to HPLC technology. Owing to the anticipated complexity of Cerro Negro composition, the significant level of detail desired in its analysis, and the unrestricted choice in separation

methodology, there was generally no justification for using less than state-of-the-art approaches or instrumentation for separations.

Theoretical efficiencies of LC columns range from ca. 500-2000 in classical LC to 50K plates/meter for HPLC. Especially in the case of HPLC, the number of plates generated per unit time--while low compared to supercritical fluid chromatography and especially gas chromatography--positively dwarfs the number obtainable with solvent extraction, precipitation, or virtually all other separation approaches viable for work on Cerro Negro. Of course, if a high degree of selectivity can be achieved, which is generally the case in a successful separation by compound class, the absolute efficiency required is typically quite low. For example, if a solvent extraction system (equations 1 and 2) could be devised for a class X with $K_p = 1000$, a single extraction (one theoretical plate) would remove 99.9% of the class from the bulk oil. However, if other classes were coextracted or K_p approached 1, many more theoretical plates would be required. Thus, other methods with potential for high selectivity should be considered, but LC has an inherent edge from the standpoint of efficiency.

Separation selectivity is too broad a topic to discuss in detail, but generally speaking, the more flexible the technique, the greater the probability of achieving the desired level of selectivity. Once again, LC possesses an inherent advantage because of the large number of modes available and variations within each mode. For example, the selectivity of virtually any solvent extraction system can be duplicated using liquid-liquid chromatography. In addition, since the stationary liquid can be chemically bonded to the support, solvent immiscibility is not a constraint with the LC approach. Interactions giving rise to precipitation can usually be duplicated using ion exchange or other modes of LC. Moreover, some effects, such as separation based on molecular size or resolution of enantiomers, are very difficult to perform via any other separation approach.

In summary, all potential separation approaches were considered, but in light of the inherent practical and theoretical advantages of LC, LC-based methods received much more attention than others. Furthermore, classical LC approaches were considered suitable only for preliminary separations where economy of materials or convenience in handling large amounts of fractions might justify their use.

Methods Based on Precipitation or Solubility Effects

Asphaltene precipitation comprises the first step in a great many separation schemes. Often this is done because the presence of *n*-alkane insolubles causes practical difficulties in subsequent steps. Since the bulk of the evidence shows the composition of asphaltene fractions to be essentially as complex and not generally distinct from the whole material (e.g, 4-6), there appeared to be no justification for their isolation from Cerro Negro. Furthermore, since the distillation residue contained 33.2% asphaltenes by weight, this fraction would have been far too large to simply ignore in the analysis, as is commonly done. Thus, one practical constraint for the separation methodology to be used for Cerro Negro is that it must be compatible with *n*-alkane insoluble material. This restriction eliminated a significant proportion of potential methods.

Precipitation of waxes is another commonly used procedure. Because of the low concentrations of *n*-paraffins anticipated in Cerro Negro (Chapter 1), this method was not investigated in detail.

Precipitation of bases with HCl gas has largely been applied to coal liquids (7-10). However, Finseth, et al. (10) found significant contamination of base fractions by phenolic compounds, and also determined that only relatively aromatic nitrogen compounds were isolated as precipitates. Furthermore, work of Martin, et al. (8) and Wallace, et al. (9) confirms the crude nature of "bases" obtained using this method. Considering the poor quality of base fractions from coal liquids, which are generally more aromatic and thus more amenable to this approach than petroleum, and the probability of acid catalyzed sample degradation during its use, HCl precipitation was not investigated further.

Solvent Extraction Methods

Isolation of acids using basic media and bases using acidic media is commonly employed for distillate fuels. While its main virtue is simplicity, it suffers from many practical and theoretical limitations. Some or all of the practical problems, such as formation of emulsions and loss of water-soluble species, can be minimized. The two greatest fundamental limitations of the approach are: the inability to extract high molecular weight acids/bases because of their inherent insolubility, even as ion pairs, in aqueous/polar organic solvents, and the inability to extract weakly acidic or

basic compounds due to the leveling effect of water on ultimate acid or base strength attainable in aqueous media.

As a generalization, the relative proportion of weaker acids/bases increases with boiling range, as does average molecular weight. Thus, the performance of extraction drops significantly on higher boiling fractions. For example, table 1 shows comparable yields for acids and bases from solvent extraction versus another method, nonaqueous ion exchange chromatography (11), on low boiling, but not high boiling, coal liquid fractions. HPLC and elemental analysis of $>370^{\circ}\text{C}$ neutrals, acids, and bases from both methods clearly showed incomplete solvent extraction of weaker acids and bases. Also, as evident in the table, extraction performed better on the $>370^{\circ}\text{C}$ fraction from the pyrolysis product, COED, than on the hydrogenation product, Synthoil. This is consistent with the much higher proportion of $>540^{\circ}\text{C}$ material in Synthoil (12), which is too high in molecular weight (hence too hydrophobic) to effectively extract. The higher ion exchange yield of SRC-II acids resulted from inclusion of pyrrolic benzologs (largely alkylcarbazoles and alkylbenzocarbazoles) in that fraction; they remained in the neutrals during extraction.

The above effects are carried to an extreme in the case of petroleum residues. For example, nonaqueous ion exchange yielded a total of 64.6 weight percent acids plus bases from Wilmington, CA, $>675^{\circ}\text{C}$ residue, compared to only 0.35 weight percent obtained by extraction (11). In related work, Buchanan (13) found phenols, indanols, hydroxybiphenyls, naphthols, anilines, other aminoarenes, and azafluorenes in a "neutral" aromatic fraction which had previously been subjected to extraction with HCl and NaOH (14). Similarly, Katoh and Ouchi (15) documented incomplete extraction of phenolic compounds, especially relatively highly alkylated species. Thus, in light of the results from internal and literature evaluations of the acid/base extraction approach, it was abandoned.

Smith, et al. (16) experimented with several unconventional extraction and precipitation agents and found widely varying recoveries of acids and bases from H-coal vacuum-still bottoms, depending on the experimental conditions and reagents employed. Unfortunately, the limited evaluation of fractions reported therein and the consideration of only one sample type prevent an assessment of the general applicability of those procedures.

TABLE 1. - Comparative acid-base-neutral yields from extraction versus nonaqueous ion exchange chromatography¹

Sample	Boiling Range (° C)	Method ²	Yield (wt %)			
			Acids	Bases	Neutrals	Total
COED Coal Liquid ³	200-370	IE	4.96	2.37	88.1	95.4
		EX	4.86	2.33	90.5	97.7
	>370	IE	3.18	2.58	94.7	100.4
		EX	0.94	2.36	96.8	100.1
Synthoil Coal Liquid ⁴	200-370	IE	25.3	6.2	68.5	100.0
		EX	20.6	7.0	69.1	96.7
	>370	IE	21.4	28.3	51.3	101.0
		EX	11.6	18.2	73.7	103.5
SRC-II ⁵	325-425	IE	25.0	10.8	65.6	101.5
		EX	15.8	10.5	72.1	98.4

¹For a description of methods and additional data, see ref. 11. Ion exchange resins were activated with methanol.

²IE = nonaqueous ion exchange. EX = extraction with aqueous-methanolic (1:2) 1 N HCl or NaOH.

³Pyrolytic coal product. See Sturm, G. P., Jr., P. W. Woodward, J. W. Vogh, S. A. Holmes, and J. E. Dooley. Analyzing Syncrude from Western Kentucky Coal, ERDA-BERC/RI-75/12, Nov. 1975, for sample documentation.

⁴Catalytic coal hydrogenation product. See Woodward, P. W., G. P. Sturm, Jr., J. W. Vogh, S. A. Holmes, and J. E. Dooley. Compositional Analyses of Synthoil from West Virginia Coal, ERDA-BERC/RI-76/2, Jan. 1976, for sample documentation.

⁵Solvent Refined Coal Product. See R. H. Harrison, S. E. Schepple, G. P. Sturm, Jr., and P. L. Grizzle, J. Chem. Eng. Data, v. 30, 1985, p. 183, for sample documentation.

Solvent extraction has also been employed for removal of "aromatics" from paraffinic oils or similar matrices (17-19). Polar solvents such as N-methylpyrrolidone and dimethyl sulfoxide in anhydrous or water-diluted states are often employed. These procedures tend not to be very selective, and thus extract many types of polar compounds, relatively condensed aromatic hydrocarbons, etc. (18). Similarly, pyridine-water extraction of heavy oils, targeted to isolate Ni and V compounds, removed only a fraction of those compounds present, resulted in coextraction of major quantities of other classes, and exhibited widely varying efficiencies between whole oils and corresponding asphaltene fractions (20,21). Thus, this type of separation, while adequate for its intended purpose in the cited work, is far too nonspecific to be used as the preliminary step in a detailed compositional analysis.

In summary, the solvent extraction approach for class separation generally suffers from 1) significant variation in partition coefficients of individual class members with structure and 2) general nonspecificity for a given class.

LC Methods

Because of its inherent advantages, LC has been extensively developed for class separations. Owing to the variety and volume of work, the various methods and approaches are grouped below for discussion.

Single Column Methods. Generally, methods employing one column strive toward simplicity while maintaining acceptable separation quality. To achieve this, typically fairly elaborate solvent programs and/or columns containing more than one type of adsorbent or column packing are used.

The simplest of these methods yields fractions of the following nominal types: saturated hydrocarbons, neutral-aromatics, and polars. Examples include classical ASTM methods, D 2549 (silica-alumina), D 2007 (clay-gel), and D 4124 (Corbett method); other classical procedures using adsorbents (22,23), and HPLC methods using silica (24,25), amino-bonded silica (26,27), and cyano-amino-bonded silica (28-30). In addition, a method referred to as SARA (saturates, aromatics, resins, and asphaltenes), which actually requires two columns, has been widely used to achieve this type of fractionation (31). All of the above require prior removal of n-alkane insolubles (asphaltenes).

Without addressing the issue of which of the above procedures produces the "best" saturate, aromatic, polar, and asphaltene fractions, some fundamental problems with this approach bear mention. First, direct analysis of the asphaltene "fraction" is virtually impossible, as discussed earlier. In addition, problems of nearly equal magnitude are encountered in analysis of a "polars" fraction. To illustrate this point, table 2 lists selected compound classes previously identified or postulated to exist in petroleum and tar sand bitumen (32-46). As indicated in the table, each homologous series, $C_nH_{2n+2}N_aS_bO_c$, represents several potential compound classes, except in the case of hydrocarbons where a, b, and c equal zero. Furthermore, with the possible exception of neutral forms, all isomeric forms of a given series would fall into the "polars" using the above approach. Because of the multitude of classes possible for each series, definitive analysis of this fraction would be virtually impossible without further separation.

TABLE 2. - Isomeric classes in petroleum¹

General Formula	Acidic Forms	Basic Forms	Neutral Forms
$C_n H_{2n+z}$	-	-	saturated and aromatic hydrocarbons
$C_n H_{2n+z} N$	pyrrolic benzologs	azaarenes, amines	N-alkylpyrroles and higher benzologs
$C_n H_{2n+z} O$	hydroxyl compounds	ketones	ethers
$C_n H_{2n+z} S$	thiols	-	thiophenic benzologs, sulfides
$C_n H_{2n+z} NO$	amides with at least one free hydrogen, hydroxylated nitrogen compounds	amides without a free hydrogen, aza- or aminoethers	-
$C_n H_{2n+z} NS$	nitrogen compounds with thiol substituents, thioamides with at least one free hydrogen, mixed thiophenic/pyrrolic types or sulfide/pyrrolic types	thioamides without a free hydrogen, aza- or aminothiophenes	-
$C_n H_{2n+z} SO$	hydroxylated thiophenes, thio-carboxylic acids	sulfoxides	mixed sulfide/ethers or thiophene/ethers
$C_n H_{2n+z} N_2$	compounds with at least one N in pyrrolic form	both N in azarene or amine functionalities	-
$C_n H_{2n+z} O_2$	carboxylic acids, diols	diones, ketoether, ester	diethers
$C_n H_{2n+z} S_2$	compounds with at least one thiol group	-	disulfides, sulfide/thiophenes, dithiophenes

¹Compiled from references 32-46.

Finally, because of the usual distribution of these types in petroleum--saturate>aromatics>polars>asphaltenes--absolute yields of asphaltenes and polars are typically quite small. Thus, either the above procedures must be scaled up tremendously* or repeated many times to obtain significant quantities of these fractions. Thus, a far more efficient approach would consist of a preliminary step which would selectively retain polar compounds from a large quantity of sample; a portion of the eluate could then be separated into saturate and aromatic fractions. Only the original SARA method (31) employs the latter strategy.

In conclusion, while useful for routine applications, separation into SARA-type fractions is an inadequate and inefficient approach for detailed analysis.

Recognition of the above shortcomings of the "four-fraction" approach led to the development of more elaborate one-column methods. Typically, a more complex series of eluents is employed to obtain several polar subfractions in these methods. Perhaps the best known procedure of this type is the method referred to as SESC (sequential elution by solvents chromatography) (47). This method and subsequent modifications have been extensively applied to coal liquids (47-51) as well as bitumens (52). This method departs from conventional liquid-solid chromatography in that it does not follow the eluotropic series concept, i.e., employ eluents of progressively stronger elution ability. For example, 3% ethanol in chloroform is used after 100% methanol, the latter is a stronger eluent in the conventional sense. Thus, the separation mechanism combines adsorption and solubility effects. Moreover, the preceding eluent modifies the surface of the adsorbent (silica), which in turn affects the behavior of the current eluent (47).

Although it was developed primarily for coal liquids, the SESC method was potentially applicable to this work. However, in-house experimentation and subsequent evaluations in other laboratories led to its rejection for the following reasons. First, separations of saturated versus aromatic hydrocarbons (fractions 1 and 2, respectively) were of very poor quality (49-53). Also, types specified for each fraction (47) generally did not correlate

*Typical absorbent/sample (W/W) ratio is 100:1.

TABLE 3. - Results from evaluation of SESC

Fraction No.	Yield, wt. %			Specified Type(s) ²	Classes Found ³
	SRC-II 325-425° C	Synthoil 200-370° C	>370° C		
1	59.9	66.8	13.7	saturates	saturates + aromatics
2	3.9	0.3	19.1	aromatics	aromatics, very weakly polar compounds (e.g., ethers)
3	19.4	17.0	27.8	polar aromatics	pyrrolic benzologs, hydroxyaromatics, aminoaromatics
4	11.6	7.3	17.0	monophenols	hydroxyaromatics, azarenes
5	1.7	3.1	3.7	basic nitrogen heterocyclics	relatively basic azaarenes
6	1.9	3.8	4.1	highly functional molecules	strongly basic or difunctional compounds
7	0.2	0.4	3.2	polyphenols	{ solvent impurities, unidentified material
8	4.6	0.2	4.8	{ increasing O content, and basicity of nitrogen	
9	0.9	0.6	4.9		
Total	104.1	99.5	108.3		

¹ Same samples as those used in table 1.

² After ref. 47.

³ Determined by HPLC, IR, and other methods as needed.

with those found, as shown in table 3. The order in elution of the various classes did match that of Farcasiu, however. Compound class assignments in table 3, as well as the overlapping of types into more than one fraction, agree well with those reported elsewhere (50,51). Thirdly, the degree of success obtained in separations with SESC and all other classical LC methods generally depends on: 1) the relative correspondence in physical and chemical properties between the particular batch of adsorbent in hand versus the one originally used to develop retention correlations, 2) operator experience, and 3) the relative match between types and amounts of compound classes assumed in the development of the method versus those actually in samples requiring fractionation. Thus, the adsorbent used by Farcasiu must have exhibited generally higher retention for most classes than the one employed in the present evaluation, for example. Compounds in the relatively heavy coal liquids investigated by Farcasiu may also have exhibited greater overall retention than the lighter coal liquids employed here. The main point is that without access to the identical adsorbent used for calibration of the method, solvents with similar levels of impurities (especially water) as those used in the development of the method, etc., the method must be essentially redeveloped in-house prior to use, and potentially will require modification for different types of samples. For example, Jacobs and Filby (52) found essentially constant levels of elemental N and S in fractions 3-9 from separation of a tar sand bitumen, which indicates complete disparity between observed versus predicted class distributions for that type of sample.

Other procedures for separating many classes from a single column have been reported. For example, methods employing from 5-15 eluents have been reported (5,42,54-57). Typically, the selection of eluents in these schemes appears to be rather arbitrary, or in some cases, Snyder's ϵ_0 data (2) are employed for eluent selection. Often, verification of the classes in each fraction is performed after the fact. Based on available correlations for silica and alumina (2,40), the chances for obtaining a series of chemically unique fractions from this approach are extremely remote, because of the extensive overlap in elution of compound classes from any single adsorbent or column packing. However, in cases where only a single class or subset of related classes is desired, one-column methods may be feasible or even preferred. For example, successful isolation of saturated hydrocarbons (58), aromatic hydrocarbon classes (27), carboxylic acids (59), and total bases (60)

has been reported using single-step, one-dimensional, separation methods. In those cases, the balance of the sample is either discarded, backflushed, or dealt with in some other analogous manner.

In-house and literature evaluations of the class-separation abilities of chemically bonded silica HPLC packings have generally shown them to be inferior to ordinary adsorbents for one-dimensional class separations (61-64).

In conclusion, the inherent simplicity of the "one-column-does-all" approach has enjoyed widespread appeal. However, until the "ultimate adsorbent," i.e., an LC column packing which possesses significantly superior class separation abilities to those currently available, becomes a reality, multidimensional separations are clearly required for comprehensive class separations of petroleum or synfuels. Furthermore, the single column approach has inherent disadvantages including the following: 1) incompatibility between *n*-alkane eluents typically needed to effect saturate-aromatic separations and samples containing *n*-alkane insolubles, 2) the need to process large quantities of most petroleums in order to obtain sufficient quantities of polar classes and other minor components, and 3) trade-offs necessary to reduce overlap between consecutively eluting classes increase in difficulty and complexity with the number of classes present. (Obviously, the worst case possible is with the whole sample and a single column.) As the result, the quality of fractions from this approach typically suffers because of the large number of compromises necessary.

Multidimensional Methods. Because of the numerous LC modes available and variations within each mode, the number of possibilities for multidimensional separation schemes is quite large. Altgelt, et al. (65) reviewed some of the more popular schemes shortly before this project began. However, little or no basis for selecting any one of those for this work was given in that review; even today, critical comparisons of chromatographic methods are quite rare (23). Thus, an in-house review of the various schemes was necessary (66-121).

As a minimum, the following information is needed to assess the effectiveness of a given scheme: mass balance over all separations, balances for CHNOS within each fraction and in total, a listing of major type(s) in each fraction, and approximate levels of other, possibly unknown, types in each fraction. Additional information of particular relevance to this project would include: Ni, V, and Fe content of fractions and balances over all separations; specific information on the distribution of sulfur-containing

classes; and known shifts in separation behavior with average boiling range. As table 4 shows, this type of information is not generally available for most published separation schemes. Thus, the applicability of most schemes in total or in part to Cerro Negro could not be objectively assessed in 1981 during the initial evaluation or even today with the additional data generated in the interim. In too many cases, "verification" of a given separation step in the schemes consisted of only cursory examination of the fractions or was based on behavior of a relatively few pure compounds which often poorly represented those present in actual petroleums. For example, GC/MS identification of a few well-resolved peaks on a broad hump of unresolved material has frequently been used to characterize the types present. The assumption that the few components identified represent the bulk of the fraction is a major one from the authors' viewpoint and requires supporting information on the total fraction for substantiation. The supporting information given is typically incomplete or totally absent.

Another common omission is lack of material and/or elemental balances. For example, virtually all of the elemental balances given in table 4 were calculated from raw data given in the cited papers; direct consideration of elemental balances in the discussion of methods is quite rare in the literature. Furthermore, the importance of such simple concepts is apparently greatly underestimated. For example, in the case where a given method is claimed to concentrate a given type, e.g., nitrogen-containing compounds, with great effectiveness, the elemental data given frequently refute the claims made. Often, the concentrate contains significant levels of the desired component, but its combined yield and elemental content fall far below the levels anticipated from the data given for the starting material. Thus, conclusions drawn from its analysis apply only to the subset actually isolated and may be totally nonrepresentative of the majority of species present.

Similarly, optimization, if any, of the separation sequence or conditions within each step is seldom addressed. In some cases, this may be due to space constraints imposed by the journal; nevertheless, experimental conditions appear to be arbitrarily selected in many cases. Thus, the work of Snyder and coworkers (2,32-34,40,85,86) appears exceptional in that class separations and adsorption chromatography in general were systematically investigated over a 10-year period.

TABLE 4. - Summary of selected multidimensional separation schemes

Method	USBM-API	Union Oil	Brigham Young University	Oak Ridge Nat'l Laboratory	University of Wyoming	Ecole Polytech.	University of Alberta
References	4, 5, 35-39, 41, 65-84	2, 32-34, 40, 85, 86	87-94	13, 14, 95-99	100-108	109-120	5,75-78,121
Applications ¹	CO, SO, Pet., HO	Pet. distillates	CO	CO, SO, Pet.	CO	Pet., HO	HO
Number & types of columns used	≥ 5 (Anion and cation exchange resins, FeCl ₃ -clay, SiO ₂ /Al ₂ O ₃ , SEC)	~20 (Anion and cation exchange resins, SiO ₂ , Al ₂ O ₃ , charcoal, Hg ²⁺ resin)	3 (Al ₂ O ₃ , SiO ₂ , PdC ₂ /SiO ₂)	4 (Aqueous extraction, Sephadex LH 20, SiO ₂ , Al ₂ O ₃)	3 (fluorocarbon, Al ₂ O ₃ , NH ₂ -bonded silica)	≥ 5 (KOH-treated SiO ₂ , HCl treated SiO ₂ , Al ₂ O ₃ , C ₁₈ -bonded SiO ₂)	4 (SiO ₂ , Al ₂ O ₃ , Ag NO ₃ -SiO ₂ , 5A mol. sieve)
Typical numbers of fractions produced	15-20	40-50	9	9	20	10-15	≥ 12
Required sample pretreatment	filtration	distillation	distillation	removal of volatiles	none	none	for C ₅ -insoluble, precoating adsorbent is required
Typical mass recovery (wt. %) obtained	≥ 95%	≥ 95%	93	77-104%	99 (92% for HPLC amino-silica separation)	NA ²	≥ 98%
Typical elemental balance obtained (wt. %)							
C	95	NA	NA	NA	95	NA	97
H	96	NA	NA	NA	101	NA	97
N	105	96	NA	NA	110	NA	≥ 130 ³
O	150	115	NA	NA	150	NA	≥ 200 ³
S	90	(sulfides not recovered)	NA	NA	NA	NA	95
Metals	90	NA	NA	NA	NA	NA	NA

¹ CO - coal liquid, SO - shale oil, Pet. - conventional petroleum, HO - heavy oil or tar sand bitumen.² NA = not available.³ Quite variable.

TABLE 4. - Summary of selected multidimensional separation schemes (cont'd)

Method	USBM-API	Union Oil	Brigham Young University	Oak Ridge Nat'l Laboratory	University of Wyoming	Ecole Polytech.	University of Alberta
Major classes isolated	Acids 3-4 acid subclasses Bases 3-4 base subclasses Neutral nitrogen Neutrals saturates monoaromatics diaromatics polyaromatics SEC ⁴ subfractions of mono-, di-, and polyaromatics	indoles carbazoles benzcarbazoles pyridines quinolines benzquinolines azaindoles azacarbazoles pyridones quinolones benzofurans dibenzofurans naphthobenzofurans dihydrobenzofurans ketones/esters hydroxyaromatics sulfoxides	Saturates Neutral-aromatics hydrocarbons thiophenic-S Nitrogen compounds 2°-N compounds aminoaromatics 3°-N compounds Hydroxyaromatics	Acids Bases azaarenes aminoaromatics Saturates Neutral aromatics polycyclic aromatics neutral nitrogen "polars"	3-4 fractions defined by solubility, which were subsequently sub-fractionated into: hydrocarbons N-compounds hydroxyaromatics polyfunctionals Hydrocarbons were subfractionated into: saturates and aromatics containing 3,5,6,7,8,9, 10-11, and 12+ double bonds	Acids carboxylic acids pyrrolic benzologs Bases 7-base subfractions Neutrals saturates polycyclic aromatics Polar compounds	Polar subfractions (3 in early work, many more in later work) Neutrals Saturates n-paraffins branched paraffins + mono- & dicyclics polycyclic alkanes Monoaromatics Diaromatics Polyaromatics
Basis for development of the method	Analysis of fractions, elution behavior of pure compounds	Extensive adsorptivity index correlations for functional groups, E° data for solvents, and pKa data.	Prior work, analysis of fractions	Prior work, analysis of fractions	Retention of pure compounds, analysis of fractions	Retention of pure compounds, analysis of fractions	Analysis of fractions
Instrumental techniques applied to fractions	MS, NMR, IR fluorescence, non-aqueous titration GC, GC/MS, elemental analysis	MS, IR, UV, nonaqueous titration	GC/MS	GC/MS	FIMS, IR, NMR, elemental analysis	GC/MS, fluorescence	Elemental analysis, UV, IR, NMR, HPLC, MS
Compound classes inadequately resolved by the method	Large polycyclic aromatic hydrocarbons contaminate acid, base, and neutral nitrogen fractions.	Most compound classes overlap into several fractions	Thiophenic sulfur compounds	Hydrophobic acids/-bases	Large polycyclic aromatic hydrocarbons	Insufficient data for evaluation	Polar fractions not well resolved or defined

⁴ SEC = size exclusion chromatography

TABLE 4. - Summary of selected multidimensional separation schemes (cont'd)

Method	USBM-API	Union Oil	Brigham Young University	Oak Ridge Nat'l Laboratory	University of Wyoming	Ecole Polytech.	University of Alberta
Compound classes inadequately resolved by the method (cont'd)	Benzologs of pyrrole and amides overlap into both acid & base fractions.						
Advantages	Demonstrated applicability to a wide range of sample types, including asphaltenes	Most definitive analysis of O- and N-containing types to date obtained with this method	Partial resolution of thiophenic sulfur compounds	Fractions suitable for Ames testing	State-of-the-Art HPLC subfractionation of aromatic hydrocarbons	HCl and KOH-treated silicas are effective for isolating strong bases and acids, respectively	Simplicity of equipment and procedures, adequate resolution of hydrocarbon classes
Disadvantages	Impurities leached from ion exchange resins	Highly complex scheme, separation of hydrocarbons not extensively discussed	Water content of adsorbents is critical. Many classes were not addressed	Extraction gives incomplete acid/base separation. Low efficiency of LH-20 column	The initial solubility-based separation greatly increases the number of fractions for analysis	Quantitative aspects of the method (yield of fractions, elemental balances, overlap of classes) cannot be assessed from the data given	Polar classes are inadequately addressed, elemental N suspect
Potential applicability to Cerro Negro	Good	Distillates only	Unknown	Poor	Unknown	Unknown	Unknown

The effect of structural variation on chromatographic behavior is seldom considered in terms of modifying experimental conditions for a given crude type/boiling range or predicting interferences or overlap of classes between fractions. For example, the retention index of nonadecylbenzene is one-half that of benzene on amino-bonded silica, an HPLC packing claimed to be relatively insensitive to substituent effects (122). Thus, in that separation, optimum cutpoints for aromatic hydrocarbon classes (1-ring, 2-ring, etc.) for higher boiling (i.e., more highly alkylated) samples may be at significantly shorter times than for low-boiling fractions with a lower degrees of alkylation. Similarly, various types of crudes could exhibit significantly different separation behavior, depending on their degree and orientation of alkylation. Furthermore, orientation and degree of substitution and the position of heteroatoms within polycyclic systems have even greater effects on the chromatographic behavior of polar compounds. Nevertheless, many separation schemes are developed and calibrated using only the simplest members of a given polar compound class, with no allowance or accounting for structural effects. Thus, it is not surprising that the distribution of a given heteroatom over the resulting fractions from separation of actual samples is often much wider than predicted from the pure compound retention data given. While not ideal, broad distributions of heteroatoms over many fractions are an inevitable consequence of the complexity of these materials; the problem is that separation results are not usually interpreted in this context and that nitrogen compounds in a fraction predesignated as an "oxygen-containing fraction," for example, are completely neglected.

Much of the available knowledge on petroleum composition was derived from the schemes in table 4 and others not considered in detail. Furthermore, those authors had different objectives and evaluation criteria than used here and have produced some excellent results. Thus, as mentioned at the start of the review, the preceding comments should not be interpreted as an overall condemnation of all preceding work. On the other hand, it appeared that a general comprehensive scheme employing state-of-the-art separation technology, which also met the stated objectives, was clearly not available.

In a direct, detailed comparison of the methods, the approach and strategy employed in the USBM-API scheme was judged the most appropriate for this work. Also, this scheme has received the widest application in terms of

the number and types of crudes and syncrudes. Reasonable mass and elemental balances were achieved with this scheme in cases where they were reported. In addition, a significant effort had been spent on overall verification and identification of deficiencies.

In summary, this approach has the following advantages:

- 1) Separation into acid, base, and neutral types effectively resolves many interfering types (see table 2).
- 2) Acidic and basic compounds, typically present in minor amounts, may be effectively isolated from large quantities of starting material with a minimum of effort.
- 3) Although the ion exchange separation itself is a relatively low resolution technique, in terms of chromatographic efficiency (plates/meter) attained, the resulting fractions are quite amenable to subsequent fractionation by state-of-the-art methodology.
- 4) Practical constraints are minimal; the methodology has been shown to work on virtually all types of fossil liquids with acceptable material balances.
- 5) The approach is suitable for separation of relatively large quantities (Kg) using laboratory scale apparatus.

Approaches based strictly on adsorption chromatography were found especially lacking in 2-5 listed above, as discussed earlier in conjunction with one-dimensional methods. Schemes utilizing extraction procedures or solubility phenomena were rejected for reasons previously discussed during evaluation of those techniques. The Ecole Polytech scheme, which was developed over the same time frame as this work, shows sufficient potential to have warranted an in-house laboratory evaluation had it been available at the start of the project. However, even today the degree of development and verification of that scheme lag considerably behind that of the USBM-API method.

Because of its widespread application, the USBM-API scheme has undergone a number of variations. For example, cyclohexane is currently more commonly used as the eluent in the nonaqueous ion exchange separation step than pentane as was specified originally (66). Also, the anion exchange resin originally

employed is no longer available. Furthermore, in some cases acids and bases are extracted from the resins in three to four steps with increasingly stronger eluents; others have extracted total acids and bases and subsequently subfractionated each in a separate step. The original method specified use of a ferric-chloride-treated clay column to remove "neutral nitrogen" or "Lewis base" compounds from the acid-base-free material. This step has frequently been omitted in more recent work. Separation of neutrals has typically proceeded via classical adsorption LC (67).

As noted in table 4, one major disadvantage of the USBM-API scheme is contamination of fractions, especially acid concentrates (79), by material leached from the ion exchange resins. This problem has only recently been addressed (11,123), and was poorly defined at the time work on Cerro Negro was initiated. Furthermore, the "accepted" substitute anion resin had never been evaluated in detail. In addition, although it was known that the order of separation of acids versus bases had a significant impact on the yield of each fraction (5), the optimum order had not been defined. The need for exhaustive elution of the ion exchange resins had also been questioned (78). Moreover, the utility of the ferric chloride clay column was in doubt, since analysis of fractions indicated substantial contamination by polycyclic hydrocarbons (124), and the composition of that fraction had never been adequately defined.

The available evidence indicates a very mediocre quality of acid/base subfractionation from sequential elution of the ion exchange resins themselves. Thus, independent separations, e.g., using alumina (35-38), are definitely superior. Furthermore, the extensive separations of neutrals via adsorption and subsequent size exclusion chromatography generate large numbers of fractions for analysis and utilize obsolete materials and approaches. Complementary procedures developed by Snyder, et al. (86) including nonaqueous ion exchange separations and subsequent separations via adsorption chromatography suffered from many of the same problems: column materials employed therein had become obsolete and were no longer available, classical LC methodology was used throughout, etc.

Therefore, although the basic strategy of the USBM-API scheme was adopted, it was felt that the separation methods themselves required significant upgrading, modernization, and additional verification. For example, development of the improved nonaqueous ion exchange procedure is discussed

below. A general effort was also made toward correcting known deficiencies in the individual separation steps or, in some cases, substituting alternate procedures. Finally, separations of selected classes not addressed in the USBM-API procedure, e.g., neutral sulfur-containing compounds, were attempted.

Summary of Nonaqueous Ion Exchange LC Separation Development

Work began with evaluation of a slightly modified version of the original method, followed by investigation of alternate procedures. Although a detailed description of the work is beyond the scope of this report, the essential findings are summarized below.

Briefly, pure compounds and a Wilmington 370-535° C distillate, which was extensively investigated in the USBM-API project itself, were employed to test the various procedures. The effectiveness of a given procedure or ion exchange resin in partitioning the pure compounds--which included acidic, basic, and neutral (ABN) types--and the Wilmington distillate, which prior work had shown to contain a great diversity of polar compound classes, was one criterion for evaluation; the others were reproducibility and yield of resin-derived impurities from blank runs.

Table 5 shows representative yields of ABN fractions from separation of the Wilmington distillate using the various types of ion exchange resins and procedures investigated. The first result, used as a benchmark in the investigation, was obtained with the original USBM-API method (66). The second result was obtained in this laboratory with the same ion exchange resins as specified in the original procedure, but the resins were not oven-dried as specified (66) and only 2.5 bed volumes of cyclohexane was employed for elution of neutrals. The latter modification was suggested by Sawatzky, et al. (78); the original method specified exhaustive elution with pentane via a solvent recycling apparatus. In spite of these modifications, agreement between the two sets of results was judged to be acceptable. Since the A-29 anion resin was no longer commercially available, the next step in the evaluation was comparison of acid yield using the "accepted" substitute, Rohm and Haas 904 anion resin. As the table shows, the acid yield dropped significantly compared to results obtained with the A-29 resin. The decrease in yield corresponded to a significantly lower effectiveness for the 904

resin, since much of the decrease could be attributed to nonretention of the weaker acids--some of which were subsequently trapped by the cation resin and thus contributed to the increased yield of the base fraction.

TABLE 5. - ABN separation yields (wt %) from Wilmington, CA, 370-535° C distillate obtained using different ion exchange resins and preparation procedures

Acids	Bases	Neutrals	Total	Notes
5.6	6.8	87.6	100.0	1
5.3	7.5	87.9	100.7	2
4.4	8.0	88.6	101.0	3
7.1	6.6	87.3	101.0	4
6.6	6.6	86.2	99.4	5,8
10.1	8.0	81.6	99.7	6,9
10.6	6.3	82.4	99.3	7
8.6	7.4	84.2	100.2	10

1. Data reported by McKay, et al. (35,36,39) using Rohm and Haas A-29 and A-15 ion exchange resins after the method of Jewell, et al. (66). They also reported 4.2% "neutral nitrogen" compounds from the FeCl₃-clay separation method.
2. Results obtained in this laboratory using a modified version of the procedure of Jewell, et al. (66).
3. Results obtained in this laboratory using Rohm and Haas 904 and A-15 ion exchange resins using the procedure of McKay, et al. (74).
4. Results obtained with the procedure of Green and Hoff (125) using BioRad MP-1 and MP-50 resins.
5. Results obtained using the procedure of Green and Hoff (125) except that diethyl ether was substituted for dichloromethane during preparation of resins.
6. Results from fully optimized procedure of Green, et al. (11).
7. Results from procedure of Green, et al. (11), except that resins were prepared using 2-propanol instead of 1-propanol.
8. Actual batch of resin used to separate Cerro Negro 425-550° C distillate. Analogous resins were used for separating 200-425° C distillate and >700° C residue.
9. Resin used to separate Cerro Negro 550-700° C distillate.
10. Results from the optimized procedure (11), except that Rohm and Haas A-29 and A-15 ion exchange resins were substituted for BioRad MP-1 and MP-5.

Overall, the performance of the ABN separation, as indicated by the first three sets of results in table 5, was unsatisfactory--especially considering the unavailability of the original anion resin. For example, elemental analysis and infrared results indicated appreciable overlap of many types into all three fractions. The resins themselves were of industrial quality and required extensive purification; moreover, their large particle size contributed to slow exchange kinetics and low chromatographic efficiency. Relatively large blanks, shown in table 6, were also obtained; thus, mass recoveries in excess of 100% probably reflect contributions from resin artifacts. For these reasons, alternates were examined. For example, adaptation of an ion exchange procedure applied to separation of acids and bases in cigarette smoke condensate (126) was unsuccessful. In addition, aqueous extraction and SESC methods were evaluated, as discussed earlier. Eventually, a search of ion exchange techniques in other application areas led to work with BioRad macroporous resins, which were of analytical quality and which were available in several particle sizes.

The BioRad resins gave increased acid and equivalent or slightly lower base yields compared to the Rohm and Haas resins, using the same procedure. Thus, a method based on their use was published (125). In that procedure, dichloromethane was substituted for benzene because the latter's carcinogenic properties were becoming widely publicized at that time. However, this substitution led to a dramatic increase in the artifact yield from the cation resin, as shown in table 6. Furthermore, mass recoveries in excess of 100% (see table 5, note 4) typically obtained with this procedure indicated significant contamination problems. Thus, a further substitution of diethyl ether for dichloromethane was made. The latter substitution proved acceptable in that equal or improved yields of acids and bases were achieved, compared to the original USBM-API method, and significantly lower analytical blanks were obtained (see tables 5 and 6, note 5). At this point, work on ABN separation of Cerro Negro distillates proceeded in earnest, and all fractions from earlier versions of the ion exchange separation were put aside.

TABLE 6. - Resin artifact yields (mg) from blank determinations on resins in table 5*

Acid Blank	Base Blank	Neutral Blank	Notes
-	-	-	1
35	25	2	2
35	25	3	3
20	120	1	4
10	10	1	5,8
15	10	2	6,9
10	10	1	7
35	35	3	10

1. Blank data were not reported by McKay, et al. (35,36,39).
2. Blanks determined in this laboratory on Rohm and Haas A-29 and A-15 resins prepared after a modified version of Jewell, et al. (66).
3. Blanks determined in the laboratory on Rohm and Haas 904 and A-15 resins prepared after McKay, et al. (74).
4. Blanks determined on BioRad MP-1 and MP-50 resins prepared after Green and Hoff (125).
5. Blanks determined on BioRad MP-1 and MP-50 resins prepared after Green and Hoff (125), except that diethyl ether was substituted for dichloromethane.
6. Blanks from fully optimized procedure (11).
7. Blanks from fully optimized procedure (11), except that 2-propanol was substituted for 1-propanol.
8. Actual batch of resin used to separate Cerro Negro 425-550° C distillate. Analogous resins were used for separating 200-425° C distillate and >700° C residue.
9. Resin used to separate Cerro Negro 550-700° C distillate.
10. Blanks from Rohm and Haas A-29 and A-15 resins prepared using the optimized procedure (11).

*Blank determinations vary significantly from batch to batch for a given type resin. A range of 50-200% of the stated value over several independently prepared lots is typical. Data reported are absolute yields from 45 mL resin packed in a 0.9 x 74-cm glass column. This quantity of resin is sufficient for retention of 1-2 g acids or bases.

Approximately midway into Cerro Negro ABN separations, the laboratory's supply of methanol became temporarily interrupted. Since large quantities of methanol were employed in the preparation of the resins, this was a serious setback. However, a significant stock of 1-propanol was located in the interim; thus, it was substituted for methanol in the resin preparation procedure. Prototype batches of 1-propanol-washed resins were evaluated via separation of the Wilmington distillate, since those results had served as a convenient measure of performance in the preliminary development work. The resulting yield of acids and bases was phenomenal, as shown in table 5. For example, nearly twice the yield of acids was achieved with the 1-propanol-washed anion resin, compared with previous batches prepared with methanol. Moreover, the neutral fraction was a brilliant yellow color, as compared to dark red/light brown fractions obtained previously. The above findings led to a complete reevaluation and reoptimization of the ABN method, which was ultimately published in 1984 (11). The effectiveness of 1-propanol versus methanol was further demonstrated by preparing batches of the original Rohm and Haas A-29 and A-15 resins with 1-propanol and obtaining significantly enhanced yields of polars from the Wilmington distillate with those resins as well, as shown in table 5 (note 10). However, the performance of the Rohm and Haas resins was still below that of the BioRad resins.

As discussed elsewhere (11), the 1-propanol-washed resins were significantly more effective in retaining very weak acids and bases than those prepared with methanol, which accounted for the increased yields of those fractions and lighter color of the corresponding neutrals. The reason for this difference in capability is poorly understood but probably reflects relative solution states of the polar groups on the resins. For example, equilibration of representative batches of anion resins with pyrrole, a weak acid, resulted in displacement of 1-3 moles of water plus alcohol per amine group on the resin. Therefore, although the resins are extensively washed with alcohol to remove water, and diethyl ether to remove alcohol, the ion exchange sites nevertheless retain coordinated polar solvent molecules. Their geometry and ease of displacement by polar compounds in the fuel or crude during separation may determine a given resin's effectiveness. In that case, the available data indicate that 1-propanol is more easily displaced than methanol.

Although preparation of the ion exchange resins was the key factor in ABN separations, other parameters were also examined. For example, the optimum separation sequence was determined to be acids first, bases second. This conclusion was drawn from pure compound studies (11), and from separation of actual samples. Figure 1 shows relatively clean partitioning of pyrrolic benzologs into the acids when they are removed first; reversing the separation order results in significant overlap of this class into both acid and base fractions.

Another extensively investigated parameter was the volume and type of solvent required for effective elution of neutrals. Extensive elution, as practiced in the original USBM-API method, resulted in carryover of weak acids and bases into the neutral fraction. The optimum volume was determined to be 2.5 times the combined void volume of the columns employed (11). Furthermore, use of too weak a solvent in elution of the neutrals resulted in incomplete elution of condensed aromatic hydrocarbons and like species into the neutral fractions, as well as contamination of acids by bases which were incompletely eluted from the anion to the cation resin during the elution of neutrals. Thus, a relatively polar solvent, a 4.5:4.5:1 mixture of benzene:tetrahydrofuran:ethanol, is required for the initial separation of petroleum residues and synthetic crudes. Use of a weak eluent such as an n-paraffin solvent results in a very high apparent yield of "acids," because of incomplete elution of bases and neutrals from the anion resin. On the other hand, once the highly polar compounds are removed in the initial step, the eluted material may be re-separated through a fresh pair of columns with a weaker solvent, 3:1 cyclohexane:benzene, to effect complete separation of weak acids and bases from the neutrals. Figure 2 shows effective isolation of relatively strong acids, e.g., hydroxyaromatics and difunctional species, in the first pass, and weaker acids, e.g., pyrrolic benzologs, in the second separation step from an SRC-II coal liquid residue boiling >325° C using the above approach.

The negative side to the concurrent development of the ABN method during work on Cerro Negro is that the procedures changed during the course of the work. Also, only one of the distillates, the 550-700° C material, was separated via the fully optimized method.

FIGURE 1. - HPLC chromatograms showing the effect of the order of anion versus cation resins on the partitioning of pyrrolic benzologs (shaded region) in Wilmington 370-535° C distillate into acid versus base fractions. (A) anion first, (B) cation first. Note the overlap of pyrrolics into both acids and bases in (B) versus quantitative retention in acids in (A). For details of the HPLC procedure, see chapter 3.

FIGURE 2. - HPLC analysis of strong and weak acid concentrates from SRC-II >325° C residue. (A) from preliminary ABN procedure using benzene eluent. (B) from optimized ABN procedure using 4.5:4.5:1 benzene:THF:ethanol. (A-1, B-1)-weak acids. (A-2, B-2)-strong acids. Key for types eluting in regions 1-5: 1-neutrals/very weak acids, 2-pyrrolic benzologs, 3-hydroxyaromatics, 4-condensed-ring hydroxyaromatics, 5-multifunctional acids (largely dihydroxy-aromatics). Note the clean partitioning of pyrrolic benzologs into the weak acids and hydroxyaromatics into the strong acids in (B). For details of the HPLC procedure, see chapter 3.

Concurrent work on improved nonaqueous ion exchange procedures in other laboratories has included one claimed to be more rapid than the original procedures (127) and another similar to the original but with the addition of a weakly basic anion resin (128). In addition, base fractions obtained by ion exchange were compared to those from other procedures (129). However, the most definitive work on factors affecting the efficiency of the ion exchange process itself as well as comparisons of various types of resins was published in conjunction with process development for shale oil denitrogenation (130,131). The latter papers led to a further improvement in the procedure for preparation of the MP-50 cation resin, discussed in Appendix 1.

Separation of Neutrals into Saturates and Neutral-Aromatics

Subsequent chapters discuss further fractionation of ABN fractions in detail. For example, in the case of neutrals (chapters 5A and 5B), fairly extensive separation into various hydrocarbon and sulfur compound classes was attempted. However, a preliminary assessment of the composition of neutrals was based on their separation into only two fractions: saturated hydrocarbons and neutral-aromatics. Fractions boiling below 550° C were subsequently analyzed by mass spectroscopy (MS). This chapter discusses the saturate/neutral-aromatic separation and presents a summary of the MS findings, which are discussed in detail elsewhere (132,133). In addition, saturate fractions from all boiling ranges were analyzed by NMR techniques (134).

Saturate/neutral-aromatic separations are typically performed via LC or HPLC using a single column--usually silica. In this work, however, a dual-column HPLC approach, using both charge transfer and adsorption modes, was employed for the following reasons:

- More complete recovery of highly condensed and/or polar aromatics was achieved over that obtained using silica alone.
- Better saturate-monoaromatic separations were obtained since the silica column was not exposed to polar eluents as would have been necessary had the total neutrals been injected onto it. In the authors' experience, once silica columns had been exposed to methylene chloride or other eluents of similar polarity, they could not be reconditioned, even with large volumes of pentane, to give a high-quality separation between saturates and hindered monoaromatics.

- The charge transfer dinitroanilinopropylsilica (DNAP) column, because of its higher capacity, could effectively separate 3-5 g of even a highly aromatic material such as Cerro Negro. Conversely, LC on plain silica columns yielded chromatograms indicating overloading with charges of only 1 g of the total neutral concentrates. Thus, the dual-column approach was actually less time consuming for processing relatively large amounts of neutrals.

- The higher chromatographic efficiency of HPLC columns resulted in significantly better separations than could be achieved using classical large-particle gravity-flow systems.

The relative merits of DNAP versus other types of column materials is discussed in chapter 5A. Briefly, it exhibits stronger retention of many aromatics than obtained with other types of column packings--including silicas bonded with amine, diamine, triamine, etc., groups. It is also relatively insensitive to variations in water content of eluents, unlike adsorbents such as alumina, and exhibits a high sample capacity, as mentioned above.

Conclusions from the Literature Evaluation and Preliminary Work

The dearth of well-established separation methods with demonstrated applicability to Cerro Negro and like materials may be generally attributed to difficulties in their fractionation as well as in analysis of the resulting fractions. LC techniques offer the best chance of success for resolution of highly complex materials because of inherent advantages in selectivity, flexibility, and efficiency. However, because of its flexibility--in terms of the number of modes available, variations within each mode, and potential combinations of several modes to achieve the desired degree of separation with the least possible effort--optimizing an LC scheme presents a formidable challenge. Single column methods seek to reduce this problem to optimization of a single chromatographic system. However, with the available column materials, fractions obtained with single column approaches are still too complex for effective analysis.

Another aspect of separation optimization is accounting for the limitations of the spectroscopic and other analysis techniques available for the chromatographic fractions. Obviously, subdivision of one unknown into

several fractions which are equally difficult to analyze accomplishes nothing. In practice, the extent of separation required to concentrate minor compound types and remove interferences depends on the sensitivity and selectivity of the analysis techniques available. Thus, since the present work places heavy reliance on MS techniques, the resulting scheme is especially designed to overcome their limitations. Since their major limitation is the inability to distinguish isomeric forms of a given empirical formula, the scheme developed for Cerro Negro specifically addresses that type of separation. For example, isolation of all the nitrogen-containing compounds in a single fraction is the least desired result possible for MS analysis, since the technique cannot generally distinguish between the various forms present. Use of special MS ionization methods, MS/MS techniques, etc., can provide some speciation of isomeric types; but clearly, if separations are to be performed at all, reduction of isomeric interference is one of their main objectives.

The current knowledge of both petroleum composition and selectivity of LC methods is inadequate to derive an optimum separation scheme from first principles. However, the literature evaluation did lead to some general guidelines. For example, an approach which initially isolates minor nonhydrocarbon classes from the bulk oil is clearly more efficient than one which attempts concurrent hydrocarbon separations as well. In the latter case, too much of the column's capacity is taken up by bulk constituents; thus, sample size must be reduced to the point where inadequate quantities of polar classes are obtained or the column must be grossly overloaded to the point where resolution suffers. Furthermore, separation into acidic, basic, and neutral types eliminates many of the potential isomeric interferences in MS analysis. For these reasons, nonaqueous ion exchange LC, or an equivalent technique, is the logical choice for the initial separation step. Similar considerations applied to further fractionation of the ABN concentrates led to additional steps in the scheme discussed in chapters 3-5.

To a good approximation, the composition of petroleums, heavy petroleums, shale oils, coal liquids, and refined products from any of these crude types may be defined in terms of ABN types and subtypes. Thus, development of a general separation approach for all sample types is technically feasible and preferred from a practical standpoint. It makes no sense to employ one

separation scheme for crudes and another for refined products. Also, too much of the recent literature has dealt with more or less "crude-type specific" separation techniques. In all probability heavy oils or syncrudes will be refined and utilized using hardware and approaches developed for conventional petroleum with only minimal modification. Therefore, it is essential that a given analysis method relate composition of "unconventional" crudes to conventional petroleum, since the latter serves as the basis for current technology. For these reasons, separation methods developed for Cerro Negro were also evaluated for suitability in separation of conventional and synthetic crudes prior to acceptance.

Finally, many of the current separation methods, especially standardized procedures, developed for conventional petroleum employ obsolete apparatus and techniques. Thus, there is a general need to modernize petroleum separation methodology as a whole. Newly developed methods should have verified material and elemental balances; the composition of each fraction should be defined within reasonable limits; in addition, practical and theoretical limitations should be specified.

EXPERIMENTAL

Apparatus

The chromatographic system for ABN separations was comprised of a pump capable of 10mL/min flow rate at 150 psi, two glass 109 by 2.5 (i.d.) cm water-jacketed columns connected in series, and a $40 \pm 1^\circ \text{C}$ water bath with circulating pump. Soxhlet extractors capable of holding glass thimbles (coarse frit) of 8 (diameter) by 22 (length) cm dimensions were employed for extraction of acids and bases adsorbed onto ion exchange resins. A 3-L round bottom flask was used in acid or base extractions. A much larger Soxhlet was used in the purification of resins. It utilized a 12-L extraction flask and held thimbles measuring 12 (diameter) by 30 (length) cm. Other equipment consisted of rotary evaporators, a vacuum oven, and miscellaneous glassware. All of the above were available from several chromatography and general supply vendors except for the glass Soxhlet thimbles, which were custom made.

Saturate-aromatic separations were done with an HPLC system comprised of two pumps (Gilson Model 302, Middleton, WI), a valve-type injector, two 30 by

2.5 (i.d.) cm columns and dual UV (ISCO Model UA-5, Lincoln, NE) and refractive index (Waters Model 404, Milford, MA) detectors. The pumps were equipped with preparative-sized pump heads capable of pumping 100 mL/min at 300 psi and were controlled via an Apple II minicomputer using Gilson-supplied software. Details of the construction of the columns are described by Vogh and Thomson (135).

Mass spectrometric analysis of saturate fractions was done using a low resolution CEC 21-103 mass spectrometer upgraded with solid-state electronics (Nuclide Corp., State College, PA). Other fractions were analyzed by high-resolution, low-voltage, electron-impact mass spectrometry using a Kratos MS-50 (Ramsey, NJ) mass spectrometer with DS-55 data system. An all-glass heated inlet system (R. J. Brunfeldt Co., Bartlesville, OK) was used for sample introduction.

Infrared (IR) spectra were obtained with a dispersive Perkin-Elmer (Norwalk, CT) Model 283 dual beam spectrophotometer. Conventional liquid sampling cells (typically 0.5 mm pathlength KBr) were employed. UV measurements were performed with a Perkin-Elmer model 200 spectrophotometer, using conventional 1 cm pathlength quartz cells.

Materials

The ion exchange resins were macroreticular styrene-divinylbenzene polymer-type bonded with strong base or acid groups. They were purchased (BioRad Laboratories, Richmond, CA) in two particle size ranges and were designated MP-1 (anion) and MP-50 (cation) by the vendor. The 200-400 mesh (37-75 μm) particle size resin was used for most of this work; 100-200 mesh (75-150 μm) particle size resins were used in separating the $>700^\circ\text{C}$ residue to avoid excessive back pressures resulting from the viscous nature of that material. Details of the ion exchange resin preparation methods appear in Appendix 1. Solvents were obtained from Fisher Scientific, Pittsburgh, PA, and were HPLC or similar grade. The extraction reagents, formic acid and 1-propylamine, were ACS reagent grade (EM-Science, Cherry Hill, NJ) and 99+% (Fluka, Hauppauge, NY), respectively. Tetrahydrofuran (unstabilized) was tested for peroxide content prior to use; only freshly opened bottles were used.

HPLC column packings for the saturate-aromatic separations were plain 60 Å 10 µm Davisil silica (Alltech Associates, Deerfield, IL), which had been heated at 125° C overnight, and dinitroanilinopropyl-derivatized (DNAP) Davisil silica, which was prepared after the procedure of Nondek and Malek (136). Reagents for preparation of DNAP-silica were purchased from Aldrich (Milwaukee, WI). Columns were slurry-packed at 3,000 psi with these materials using carbon tetrachloride as the slurry solvent and pentane as the driving solvent.

IR solvents (dichloromethane, 1,2-dichloroethane, carbon tetrachloride) were of spectrophotometric grade and stored over MgSO₄ to maintain dryness.

Methods

ABN Separations. With the exception of the method for preparation of ion exchange resins previously discussed in the Introduction, the ABN procedure generally was that of Green, et al. (11). The amounts of material charged to the columns were nominally 250, 170, 110, and 125 g for the 200-425°, 425-550°, 550-700°, and >700° C boiling ranges, respectively. The distillate or residue was dissolved in sufficient eluent for an overall charge volume of 650-750 mL. Eluents employed for the different boiling ranges are specified in figures 3 and 4. The nominal 700 mL charge volume was selected because it represented at least a 2:1 (V/V) solvent to sample ratio and was approximately equal to the total void volume of the pair of ion exchange columns (670 mL). The latter was determined by measuring the retention volume of pentane through a set of anion and cation columns connected in series. The total volume of eluent needed to elute the neutrals was also based on the system void volume. As shown previously (11), 2.5 void volumes (1675 mL) was sufficient for elution of neutrals. After elution of both columns, an additional 335 mL of eluent (half the void volume of both columns) was pumped through the cation column only (placed second) to flush out a minor amount of neutrals which may have been eluted from the anion column and thus contained in the void volume of the cation column.

FIGURE 3. - Scheme for ABN separation of distillates.

FIGURE 4. - Scheme for ABN separation of the residue.

The eluents used for the elution of neutrals from the 550–700° C and >700° C boiling ranges were somewhat weaker than those recommended in the optimized procedure (11). In the latter, 25% benzene–75% cyclohexane is recommended for elution of 550–700° C neutrals instead of pure cyclohexane as used here, and 45% benzene–45% tetrahydrofuran–10% ethanol for separating strong acids and bases from >700° C residue instead of pure benzene as used here. Weak acids and weak bases were subsequently separated from the >700° C material using the optimum eluent, 3:1 cyclohexane:benzene (figure 4). However, the weak acid/base separation required two passes, designated I and II, because of apparent column overloading in pass I.

Adsorbed acids and bases were Soxhlet-extracted overnight as described earlier (11). For extraction of acids, the Soxhlet pot was filled two-thirds full with benzene, and 110 mL formic acid was added. Extraction of acids was achieved via the benzene–formic acid minimum-boiling azeotrope. For extraction of bases, a 2-neck extraction flask was used, and an addition funnel filled with 125 mL of *n*-propylamine was used to slowly add the amine to the benzene in the pot over a period of several hours. In the case of the >700° C strong acids and bases, approximately 250 mL of tetrahydrofuran (THF) was also added to the Soxhlet pot. THF promoted extraction of very high-boiling, highly polar materials.

ABN fractions were recovered using a rotary evaporator to remove solvent. For acid and base fractions, additional benzene was added near the end of solvent removal to aid in removal of entrained water as the minimum-boiling benzene–water azeotrope. For fractions boiling above 425° C, a vacuum drying oven at 60° C was used to take fractions to constant weight. In the case of 200–425° C fractions, solvent was removed down to levels of 1–5% by weight; the remaining solvent was determined by gas chromatography and its weight subtracted to calculate net yields, as described elsewhere (11). The latter procedure minimized losses of volatile sample components during solvent removal.

Saturate-Aromatic Separations

Aliquots of neutral concentrates were dissolved in a 4:1 excess (V/V) of hexane and injected onto the DNAP HPLC column. For lower boiling neutrals, up to 5 g was injected; charges of >700 neutrals were near 3 g. Elution of saturates plus some monoaromatics through the DNAP column was achieved using

pentane or hexane as the eluent. Higher ring aromatics plus any polar compounds in the neutrals were recovered by subsequent backflushing with 30% pentane-70% methylene chloride until the ultraviolet (UV) detector returned to baseline. Toluene was used as a retention marker for the elution of saturates plus monoaromatics. The saturate-monoaromatic separation of the first fraction from the DNAP column was achieved using a silica column. Nearly solvent-free, saturate-plus-monoaromatic fractions were redissolved in a 4:1 excess of pentane and injected onto the silica column. Pentane was used as the eluent for this separation, and both UV and refractive index (RI) detectors were used to monitor the separation progress. The cut point for saturates versus monoaromatics was defined as the point where the UV detector (254 nm) trace began to rise significantly above baseline and the RI detector indicated nearly complete elution of saturates. At this point, flow through the column was reversed, and monoaromatics were recovered by backflushing with pentane. For this work, monoaromatics were recombined with higher ring aromatics obtained from the DNAP column for a total neutral-aromatic fraction.

Mass Spectrometric Analysis of 200-425° C and 425-550° C Acid, Base, Saturate, and Neutral-Aromatic Concentrates

Saturates were analyzed by the ASTM standard method D 2786. Samples of each saturate fraction were introduced into the reservoir of the inlet system of the mass spectrometer by heating (300° C) known amounts (0.5-1.0 mg) sealed in indium tubing in the external glass cup injector.

The neutral-aromatic, acid and base fractions from 200-425° and 425-550° C distillates were analyzed by high-resolution, low-voltage, electron-impact mass spectrometry (HR/LV/EI/MS). Spectra were acquired at ca. 40,000 and 65,000 dynamic resolving power with a scan rate of 1000 seconds per decade starting from mass 700. The electron energy used in generating 40,000 and 65,000 resolution spectra produced approximately 20:1 and 10:1 ratios for m/z 106 to m/z 91 for *p*-xylene, respectively. Approximately 8 mg of 200-425° C distillate fractions or 10 mg of 425-550° C distillate fractions was introduced into the mass spectrometer. Inlet system and source temperatures were 300° C for samples from the 200-425° C distillate fractions and 325° C for 425-550° C fractions. At least 99% of all samples was volatilized. Mass calibration was accomplished by introduction of a mixture of halogenated aromatic compounds simultaneously with the sample. The calibration mixture

was similar to that previously reported by Aczel and coworkers (137). The mass and intensity data were transferred to a DEC 11/70 computer via magnetic tape for assignment of most probable formulas based on the experimental masses after the method of Scheppele, et al. (138,139). The molecular ion intensities were corrected as necessary for contributions from unresolved ^{13}C isotope peaks. In cases where homologous series exhibited masses systematically intermediate between masses of ions differing in composition by C_3 and SH_4 , ion intensities were partitioned between the two compound types assuming that the observed mass of the unresolved doublet was equal to the weighted average of the masses of the two components with the fractional intensities as weighting factors, $M_{\text{obs}} = M_1 (I_1/I_t) + M_2 (I_2/I_t)$. Carbon number distributions, average molecular weights, and elemental compositions were calculated assuming equal mole-sensitivity for all compounds in a given fraction.

Other Analyses

Methods for elemental analysis (C, H, N, O, S, Ni, V, and Fe) of fractions were the same as those described in chapter 1 for whole distillates/residues/crudes. Methodology for determination of average molecular weights also appears in chapter 1. Details of the qualitative and quantitative interpretation of infrared spectra are discussed in chapter 3, and elsewhere (140).

RESULTS AND DISCUSSIONS

The ABN separation largely accomplished the following goals: 1) isolation of polar compounds from bulk neutral constituents, 2) effective partitioning of polars into acidic and basic groups, and 3) quantitative mass and elemental recovery. Similarly, saturate and neutral-aromatic fractions obtained from whole neutrals showed minimal overlap of the two types between the respective fractions, and quantitative mass and elemental recoveries.

However, the limitations in the techniques available for analysis of the fractions prevented rigorous assessment of their detailed composition in most cases. Thus, considerable subjective interpretation of the available data was necessary in the evaluation of the quality of fractions obtained, and for some compound classes, no definite conclusions concerning separation behavior or concentration in Cerro Negro were possible. Furthermore, since the terms

"acidic," "basic," and "neutral" have no rigorous definition, the separation process itself effectively classifies each compound type accordingly. Therefore, the most useful criteria for evaluating the ABN separation's effectiveness are 1) its relative ability to partition all members of a given class into a single fraction and 2) its minimization of analytical interferences via resolution of interfering classes into different fractions. Evaluation of the saturate/neutral-aromatic separation was more straightforward because of the ease in defining the chemical distinction between those types. Finally, in many cases further separations described in subsequent chapters were needed to adequately define the effectiveness of these primary separation steps.

Mass and Elemental Balances

Tables 7 and 8 show mass and elemental balances, respectively, from the separations. Corresponding data for metals (Ni, V, and Fe) are discussed in chapter 6. Briefly, recovery of Ni and V was near 90%, and that of Fe was much lower, owing in part to particulate forms of the latter. Mass recovery over both the ABN and saturate/neutral-aromatic separations was essentially quantitative for the distillates and nearly so (97.7 wt. %) for the residue. Similarly, balances calculated for C, H, N, and S corresponded well with data on the starting materials. However, the recovery of oxygen was invariably too high, by up to a factor of two.

As discussed in the Introduction, poor oxygen balances are a chronic problem for chemical separations in general. Sources of error include incomplete removal of water and oxygen-containing solvents, and sample oxidation during handling. To illustrate the magnitude of the problem, samples of 200-425° C and 425-550° C bases were resubmitted for oxygen and water (Karl Fisher) in 1987 for comparison to data in table 8, which were obtained in 1983. Oxygen content increased from 3.09 to 3.66 wt % for 200-425° C bases and from 1.33 to 1.97 wt % for the 425-550° C bases over the four-year period. Water content was not determined in 1983, but was 0.76 and 1.34 wt % for the 200-425° and 425-550° C bases, respectively, in 1987. Both samples were stored in vials with plastic Polyseal® lids, which are permeable to both air and moisture. Given this tendency toward oxygen, and perhaps, water uptake over time in a closed container, it is safe to assume that extreme precautions would be necessary to achieve acceptable oxygen balances from any separation procedure.

Table 7. Mass Balances of Separations.

Boiling Range, °C	Yield, Weight Percent of Distillate ¹						Total Saturates & Aromatics	Total Recovery ²
	Acids	Bases	Neutrals	Total ABN	Saturates	Neutral- Aromatics		
200-425	3.17 ± .06	1.15 ± .10	94.5 ± .2	98.8 ± .2	38.9 ± .3	55.8 ± .6	94.7 ± .7	99.0 ± .8
425-550	6.87 ± .02	4.14 ± .10	89.2 ± .1	100.2 ± .2	20.6 ± .6	68.0 ± .9	88.6 ± .7	99.6 ± .8
550-700	12.3 ± .9	10.3 ± .8	78.1 ± .5	100.7 ± .5	9.9 ± .2	67.7 ± .2	77.6 ± .2	100.2 ± .6
>700								
Strong	21.0 ± .6	23.8 ± .7						
Weak-I	7.4 ± .3	6.3 ± .2						
Weak-II	4.2 ± .4	3.8 ± .1						
Total	32.7 ± .	35.7 ± .2	31.5 ± .1	97.9 ± .2	1.18 ± .02	30.1 ± .2	31.3 ± .2	97.7 ± .3
Yield, Weight Percent of Whole Crude								
--	18.2	17.6	62.0	97.8	14.7	46.9	61.6	97.4 ³

¹Results shown are mean ± average deviation from 2-4 separations in the case of ABN, and mean ± standard deviation from 10-20 separations of saturates and aromatics.

²Total recovered over both ABN and saturate-aromatic separations.

³Total recovery for whole crude includes losses from distillation (1.22 wt %). Distillate on yields were (wt % of crude): 2.59 (<200° C), 22.42 (200-425° C), 15.80 (425-550° C), 12.61 (550-700° C), and 45.36 (>700° C)

TABLE 8. - Elemental analysis of selected ABN fractions.

Boiling Range, °C	Fraction	Weight Percent						Total
		C	H	H/C ¹	N	O ²	S	
200-425	Whole Dist.	84.86	11.61	1.631	0.091	0.13	2.90	99.59
	Acids	78.60	9.88	1.498	0.66	8.84	1.36	99.34
	Bases	79.85	9.69	1.446	4.05	3.09	2.75	99.43
	Neutrals	85.45	11.65	1.625	0.023	<0.1	2.93	100.05
	ABN-Balance ³	84.30	11.46	1.620	0.09	0.31	2.85	99.01
	Saturates	86.31	13.63	1.882	<0.01	<0.1	0.010	99.95
	Aromatics	84.38	10.37	1.465	0.048	0.14	4.90	99.84
	S-A Balance ³	85.34	11.74	1.640	0.028	0.08	2.90	100.08
425-550	Whole Dist.	84.58	10.92	1.538	0.34	0.45	3.46	99.66
	Acids	79.09	9.60	1.447	1.25	6.21	2.43	98.58
	Bases	82.91	9.66	1.388	3.09	1.33	3.05	100.04
	Neutrals	84.92	11.11	1.560	0.14	0.14	3.72	100.03
	ABN-Balance ³	84.61	10.97	1.545	0.34	0.62	3.61	100.15
	Saturates	86.64	13.37	1.839	<0.01	<0.1	0.024	100.01
	Aromatics	84.28	10.42	1.473	0.18	0.15	4.79	99.80
	S-A Balance ³	84.24	11.03	1.548	0.14	0.11	3.66	99.18
550-700	Whole Dist.	84.35	10.77	1.521	0.50	0.55	4.01	100.18
	Acids	81.09	9.17	1.347	1.33	3.95	3.42	98.96
	Bases	80.94	9.38	1.381	2.22	1.58	3.49	97.61
	Neutrals	84.63	11.09	1.562	0.17	0.18	4.01	100.08
	ABN-Balance ³	84.66	10.79	1.518	0.52	0.79	3.92	100.68
	Saturates	86.33	13.56	1.872	<0.01	<0.1	0.013	99.90
	Aromatics	84.26	10.80	1.527	0.20	0.22	4.58	100.06
	S-A Balance ³	84.02	11.09	1.562	0.17	0.19	3.97	99.44
>700	Whole Resid	83.65	9.28	1.322	1.16	0.89	4.56	99.54
	Strong Acids	81.49	8.18	1.197	1.71	2.21	4.47	98.06
	Weak Acid-I	80.59	8.52	1.260	1.22	4.09	4.42	98.84
	Weak Acid-II	77.75	8.36	1.281	1.08	8.88	3.96	100.03
	Strong Bases	83.09	8.36	1.199	1.80	1.05	4.59	98.89
	Weak Base-I	81.86	9.02	1.313	1.33	1.74	5.33	99.28
	Weak Base-II	82.11	9.49	1.377	1.07	1.07	5.12	98.86
	Neutrals	84.50	10.87	1.533	0.33	0.17	4.18	100.05
	ABN-Balance ³	80.76	9.02	1.331	1.14	1.63	4.36	96.91
	Saturates	86.28	13.61	1.880	<0.01	0.13	0.019	100.02
	Aromatics	84.16	10.85	1.536	0.36	0.45	4.07	99.89
	S-A Balance ³	83.50	10.86	1.535	0.34	0.43	3.88	99.01

¹Atomic ratio.²Direct determination.³These data are not corrected for incomplete sample recovery from separations. ABN- and S-A balances were calculated from elemental content of individual fractions and fraction yields (table 7).

Mass balances for individual separations used in the computation of averages for table 7 are compiled in Appendix 2. Also included in the appendix are selected data from prototype versions of the ABN separation procedure. Since further separations were performed on selected ABN fractions from early procedures, those data are needed to facilitate understanding of results presented in later chapters. In addition, comparison of early versus later results documents the significant improvement achieved in the ABN method over the course of its development. Finally, results from separation of the 425-550° C distillate and >700° C residue using the current version of the ABN method are provided for comparison. These recent data are not included in the main body of the report because the resulting fractions have not been analyzed.

Overall precision of the chromatographic yields in table 7 was excellent. However, in general, precision of relative acid and base yields decreased with increasing boiling point. The major cause of greater variation in yields from higher boiling fractions is increased levels of weakly polar species which can behave either as acids or bases. Thus, the precision in the sum of acids plus bases was equivalent through all boiling ranges, whereas the relative scatter in individual acid and base yields increased with boiling point (Appendix 2) as slight variations in actual separation conditions caused variable partitioning of the compounds between acid and base fractions.

In terms of Cerro Negro composition, table 7 shows that relative acid content increases with boiling range, base content increases even more than acid content, and saturates decrease from nearly 40% in the 200-425° C distillate to slightly over 1% in the >700° C residue. Neutral-aromatics are relatively constant (56-68%) in the distillates but drop to 30% in the >700° C residue. Results on a whole crude basis show that nearly half of Cerro Negro is neutral-aromatics, with the balance fairly equally divided between acids, bases, and saturated hydrocarbons. H/C ratios (table 8) generally increase in the order: acids=bases<neutral-aromatics<saturates. In lower boiling distillates, acid H/C ratios were higher than those of corresponding bases because of relatively saturated acidic types such as saturated carboxylic acids. However, in the 550-700° C and >700° C boiling ranges, bases had a slightly higher H/C ratio than acids. H/C ratios of saturates were virtually constant over all boiling ranges, with an average value near 1.87. Neglecting

effects of aromatic impurities on H/C, the data obtained indicate predominantly cyclic saturates with an average of 2.1, 3.5, 3.9, and 4.0 rings per molecule for the 200-425°, 425-550°, 550-700°, and >700° C boiling ranges, respectively. These estimates are in reasonable agreement with NMR-calculated results (134).

While carbon and hydrogen are conveniently expressed as H/C ratio, comparison of other elements is more meaningful on a molecular basis. Thus, elemental N and S content in table 8 were used to calculate distributions of N- and S-containing compounds over the distillation and chromatographic separations:

$$W_y = (W_x)(\overline{MW}/\text{At.Wt.}_x), \quad (3)$$

where: W_y = wt % of compounds in fraction y which contain x;

W_x = wt % of the element x in fraction y;

$\overline{MW}$ = average molecular weight of fraction y (see chapter 1); and

At.Wt._x = atomic weight of x, where x = N or S.

and,

$$F_y = (W_x/W_d)(Y) \quad (4)$$

where: F_y = fraction (wt %) of the total x in a given distillate contained in fraction y;

W_d = wt % x in the whole distillate; and

Y = yield (wt %) of fraction y from the distillate (table 7).

Given their low levels of S and N, W_y and F_y were not calculated for saturate fractions. Results for other fractions are summarized in tables 9 and 10.

Table 9. Distribution of nitrogen compounds in ABN and neutral-aromatic fractions¹.

Boiling Range, °C	Weight Percent Fraction as N-Compounds (W _y)					Percent of Total N-Compounds in each Fraction (F _y)				
	Whole Distillate	Acids	Bases	Neutrals	Neutral- Aromatics	Acids	Bases	Neutrals	Neutral- Aromatics	ABN- Balance
<200	0.025	-	-	-	-	-	-	-	-	-
200-425	1.74	14	86	0.44	0.89	23	51	24	29	98
425-550	9.4	34	88	3.9	4.7	25	38	36	36	99
550-700	17.2	45	84	5.7	6.7	33	46	27	27	106
>700										
Total	83	99	135	22	24	43	48	9	9	100
Strong	-	107	143	-	-	31	37	-	-	-
Weak-I	-	85	120	-	-	8	7	-	-	-
Weak-II	-	84	101	-	-	4	4	-	-	-

¹One nitrogen per molecule was assumed for these calculations.

Table 10. - Distribution of sulfur compounds in ABN and neutral-aromatic fractions¹.

Boiling Range, °C	Weight Percent Fraction as S-Compounds (W _y)					Percent of Total S-Compounds in Each Fraction (F _y)				
	Whole Distillate	Acids	Bases	Neutrals	Neutral- Aromatics	Acids	Bases	Neutrals	Neutral- Aromatics	ABN- Balance
<200	5.6	-	-	-	-	-	-	-	-	-
200-425	24	13	26	25	40	1.5	1.1	94	94	97
425-550	42	29	38	45	55	4.8	3.6	96	94	105
550-700	60	50	58	59	67	10.5	9.0	78	77	98
>700										
Total	142	127	175	124	121	31	36	29	27	96
Strong	-	123	159	-	-	20.6	24.0	-	-	-
Weak-I	-	134	209	-	-	7.2	7.4	-	-	-
Weak-II	-	134	211	-	-	3.6	4.3	-	-	-

¹One sulfur per molecule was assumed for these calculations.

Equations (3) and (4) were not generally applicable to elemental oxygen data for two reasons. First, as discussed previously, oxygen balances over ABN separations were poor. Secondly, infrared evidence indicated that oxygen in acid fractions was largely present as carboxylic acids which, of course, are O_2 compounds. Thus, the following equation was used to calculate the wt. % of an acid fraction (W_{acids}) consisting of oxygen (O_2) compounds:

$$W_{acids} = (wt. \% O_{acids})(\overline{MW}/32), \quad (5)$$

where 32 represents 2 times the atomic weight of oxygen. W_y for bases, neutral-aromatics, and whole neutrals was calculated using equation (3). W_t for the whole distillate or residue was computed from the weighted sum of W_y 's of the fractions, which was then corrected by the ratio (R) of the directly determined versus ABN-Balance elemental oxygen contents in table 8:

$$W_t = (W_{acids} \times Y_{acids}/100 + W_{bases} \times Y_{bases}/100 + W_{neutrals} \times Y_{neutrals}/100) \times R. \quad (6)$$

It should be noted that although W_t was corrected for high recovery of elemental oxygen via multiplication by the factor "R," W_y results for the individual fractions were not similarly corrected and thus reflect contributions from air oxidation and/or contaminants.

Individual values of F_y for oxygen ($F_y(O)$) over all fractions were effectively normalized to 100% via their calculation using equation (7):

$$F_y(O) = (W_y/W_t)(Y)(R). \quad (7)$$

In any case, although the above method of calculation appeared the best possible in view of the shortcomings of the elemental oxygen data, it should be recognized that the results summarized in table 11 are, at best, approximations.

Table 11. - Distribution of oxygen compounds in ABN and neutral-aromatic fractions¹.

Boiling Range, °C	Weight Percent Fraction as O-Compounds (W _y)					Percent of Total O-Compounds in Each Fraction (F _y)				
	Whole Distillate	Acids	Bases	Neutrals	Neutral- Aromatics	Acids	Bases	Neutrals	Neutral- Aromatics	ABN- Balance ²
<200	-	-	-	-	-	-	-	-	-	-
200-425	1.9	81	58	<1.7	2.3	57	15	28	28	-
425-550	6.8	73	33	3.4	3.4	53	15	32	25	-
550-700	12	58	52	5.3	6.5	43	32	25	26	-
>700										
Total	37	106	87	10	27	52	44	5	12	-
Strong	-	61	73	-	-	19	26	-	-	-
Weak-I	-	124	137	-	-	14	13	-	-	-
Weak-II	-	302	88	-	-	19	5	-	-	-

¹One oxygen per molecule was assumed for all fractions except acids which were assumed to be O₂ compounds.

²Because the method used to calculate O-compound distributions effectively normalized results to 100%, actual ABN-balances were not determined.

Results in tables 9, 10, and 11 carry implicit assumptions: 1) mono-functionality, except for oxygen in acid fractions where O_2 -forms were assumed, 2) uniformity in molecular weight distributions for all heteroatomic compounds within a given boiling range, and 3) in the case of oxygen, validity of the data normalization approach employed. However, several conclusions were clearly beyond uncertainties resulting from those assumptions.

- Each element distributed over all three ABN fractions. For example, one-half or less of the total nitrogen compounds partition into the base fractions, even though N is classically thought of as a "basic" element. Similarly, only about one-half of the oxygen compounds were isolated as acids; the balance being split between bases and neutrals. The distribution of sulfur compounds closely follows gravimetric yields of the fractions, thereby indicating uniform incorporation of S into ABN types.
- The relative concentration of nitrogen-containing compounds in acid fractions increases significantly with boiling point. For example, only 14% of the 200-425° C acids contain nitrogen, whereas, on the average, every >700° C acid molecule contains one nitrogen. The percent of total nitrogen compounds in each boiling range which is present in acid fractions also rises with increasing boiling point. For example, 23% of nitrogen compounds in the 200-425° C distillate exhibit acidic behavior, whereas 43% of the >700° C nitrogen compounds partitioned into acidic fractions.
- The percent of distillable bases containing nitrogen is relatively constant, ranging from 84-88%. Nondistillable bases contain more than one nitrogen atom per molecule, on the average, with nitrogen decreasing in the order: strong>weak-I>weak-II bases.
- Although nitrogen compounds are a minor constituent of the bulk neutral fractions, except for >700° C neutrals where 24% of the neutral-aromatics contain nitrogen, the neutral/neutral-aromatic fractions as a whole still hold a significant proportion of the total nitrogen compounds in a given boiling range due to their high overall proportion of the total distillate. The percentage of nitrogen compounds

exhibiting "neutral" separation behavior is lower for the residue than the distillates, which typically contain 30% of the total nitrogen compounds present as compared to only 9% for the residue.

- Compared to the average for the whole distillate/residue, acid fractions are generally slightly deficient in sulfur-containing compounds and neutral-aromatics are somewhat enriched. The only striking variation in sulfur distributions occurs in the $>700^{\circ}\text{C}$ residue where the base fractions are significantly enriched in sulfur-containing compounds compared to the other fractions, which was not the case for any of the distillates.
- The decreasing proportion of distillate acids containing oxygen with increasing boiling range parallels the previously mentioned increase in nitrogen-containing acids. The apparent ratios of oxygen- and nitrogen-containing compounds for the $>700^{\circ}\text{C}$ acids are subject to great uncertainty. However, taken at face value, strong acids contain slightly over one nitrogen per molecule and 61% "O₂-types" or essentially an equivalent level of oxygen. The level of nitrogen compounds decreases slightly for weak acids while their apparent oxygen content increases tremendously, up to an equivalent of three O₂-groups per molecule for the $>700^{\circ}\text{C}$ weak-II acid fraction.
- Based solely on elemental data, the compositions of distillate fractions may be approximated as follows: Acids: predominantly oxygen compounds in lower distillates, but with increasing proportions of nitrogen-containing compounds at higher boiling ranges. Bases: about 85% nitrogen compounds, with the balance comprised of O- or SO-types. Neutral-aromatics: 2-3% N/O compounds in lower boiling ranges up to 10-12% in the highest boiling distillate, with the balance being more less equally split between aromatic hydrocarbons and neutral sulfur-containing species. Acids and bases in the residue contain approximately one nitrogen and a total of three oxygen/sulfur atoms per molecule, for a total of four heteroatoms per molecule. At least one of these nominally imparts a net acidic or basic character to compounds in the respective fractions. Nondistillable neutral-aromatics contain

1.2 sulfur atoms per molecule on the average, with 50% containing an additional N or O atom.

From a practical standpoint, separation of 0.5 kg of each distillate and the residue in two to four runs using conventional apparatus, with a minimum of experimental difficulty, and achieving acceptable material and elemental balances are significant accomplishments for the ABN method. The saturate/neutral-aromatic separation appears equally successful from this viewpoint. However, to satisfy the stated objectives, more detailed analysis of the fractions was needed in order to determine the degree to which the observed heteroatom distributions and other data actually reflect partitioning of different classes into each fraction, rather than chromatographic overlap of a single class into two or more fractions.

Further Analysis of Saturate Fractions

The main objective of saturate fraction analysis was determination of levels of aromatic contaminants. However, a general characterization of their composition was also performed.

Since both UV and refractive index (RI) detectors were employed for monitoring the HPLC separations, at least qualitative assessment of the degree of saturate-aromatic overlap was possible from inspection of the chromatograms themselves. Figures 5-7 illustrate the degree of resolution obtained in both the preliminary DNAP separation, which isolates saturates plus monoaromatics from polycyclic neutrals, and the subsequent saturate/monoaromatic split obtained on the silica column. Resolution of saturates plus monoaromatics from higher ring-number species is more easily visualized when the DNAP column is operated in the forward flow mode, at least past the point where diaromatics elute. Figure 5 shows the corresponding chromatogram obtained for the 200-425° C neutrals. Figure 7A shows the equivalent result when backflushing is initiated immediately after elution of the saturates plus monoaromatics. Although the same degree of resolution is obtained in both cases, it is more clearly illustrated in figure 5. Similarly, figure 6 shows baseline separation between individual saturate and monoaromatic species in the forward flow mode. However, the saturate/monoaromatic split obtained from separation of an actual sample is never as complete as implied by figure 6.

FIGURE 5. - DNAP separation of 0.1 g 200-425° C neutrals, using forward elution for monoaromatics + saturates and diaromatics, and backflush mode for elution of >2-ring aromatics. Solvent program: 100% n-pentane for 5 min, followed by a linear gradient from 100% n-pentane to 70% n-pentane: 30% dichloromethane in 25 min. Flow: 30 mL/min.

FIGURE 6. - Isocratic separation of n -heptadecane and toluene on silica.
 n -Pentane solvent, 20 mL/min.

FIGURE 7. - (A) Initial separation of saturates + monoaromatics from ≥ 2 -ring compounds from 425-550° C neutrals on DNAP. (B) Reseparation of first fraction in (A) on silica to obtain saturates and monoaromatics. The second fractions from (A) and (B) were recombined to obtain neutral-aromatics. See Experimental for separation conditions.

Thus, as shown in figure 7B, significant UV response is typically observed at the saturate-monoaromatic cutpoint. Hence, some overlap of monoaromatic species into the saturate fraction invariably occurred. The chromatograms shown are representative of those obtained for all boiling ranges, except that the monoaromatic-diaromatic valley became less distinct as the boiling point increased. However, this had little practical effect on the quality of the saturate/neutral-aromatic separation.

Although the HPLC chromatograms confirm some overlap of aromatics into the saturate fraction, they are not a useful basis for quantitative assessment nor do they directly reveal the extent of saturate contamination of aromatics. In fact, no direct means for assessing the latter could be devised. However, based on the assumptions that no net retention of saturates occurred and that they exhibited peak shapes analogous to that shown for *n*-heptadecane in figure 6, the cutpoint selected should have effected equal degrees of overlap between saturates and monoaromatics in each boiling range. Also, since the total quantity of neutral-aromatics was always greater than that of the monoaromatics, the net degree of contamination of neutral-aromatics by saturates should have been less than the corresponding case for saturates.

Contamination of saturates was independently assessed by UV, MS, and NMR techniques. In the NMR experiments, only the aromatic protons and carbons from benzene, used in the transfer of saturate fractions, were detected (134). ASIM D 2/86 MS analysis of 200-425° C and 425-550° C saturates indicated no monoaromatics in the 200-425° C saturates and 3.3 wt % in the 425-550° C saturates (132). A summary of those results is given in table 12. However, the accuracy of those data is suspect, because both NMR and GC/MS data show the combined level of normal and iso paraffins, "zero-ring" saturates, to be one to two orders of magnitude less than indicated in the table (134). Moreover, there is no reason to assume any greater reliability in the data for monoaromatics. The D 2786 method incorporates implicit assumptions which probably make it inapplicable to Cerro Negro saturates or similarly *n*-alkane deficient samples.

TABLE 12. - Analysis of the Cerro Negro saturates
by ASTM method D 2786

Compound Type	Saturates, Volume Percent	
	200-425° C	425-550° C
0-ring	11.3	6.0
1-ring	22.0	21.1
2-ring	32.0	21.6
3-ring	21.0	24.2
4-ring	13.8	15.7
5-ring	0	5.8
6-ring	0	2.3
MA ¹	0	3.3

¹Monoaromatics.

UV determination of aromatics in saturates was based on calibration factors derived from UV spectra of monoaromatic fractions from the corresponding boiling range. Isolation of monoaromatics is discussed in chapter 5A; all measurements were made at 254 nm. Table 13 shows results for monoaromatic carryover into saturates determined by the UV method. The apparent increase in aromatic contamination with boiling point closely parallels the corresponding decrease in the ratio of saturate versus neutral-aromatic yields (table 7). The inverse correlation between yield of saturates and their purity fits classical chromatographic theory which predicts equal contamination for overlapping peaks of equal area, but increasingly greater contamination of the smaller peak as the area ratio increases. Nevertheless, the presence of only 4.2% aromatics in the >700° C saturates represents a good quality separation, considering that the >700° C neutrals contained only 3.8% saturates and 95.5% aromatics. The accuracy of the UV data largely depends on the purity of the monoaromatic fractions used for calibration, and the assumption of equal response for monoaromatics overlapping into saturates versus that of the whole monoaromatic concentrates. Although neither of the above could be absolutely evaluated, the results in table 13 are probably within a factor of two of the true result. Also, given the molecular weights of saturate fractions specified in chapter 1, the concentrations of monoaromatics in the table would provide very low concentrations of aromatic hydrogen and carbon for detection by NMR, which explains their lack of detection with that technique.

TABLE 13. - Monoaromatic contamination of saturates
as determined by UV absorbance at 254 nm

Boiling Range (° C)	Monoaromatics (wt %)
200-425	1.3
425-550	2.0
550-700	3.1
>700	4.2

The quality of the saturate/neutral-aromatic separation is ultimately limited by the ability of the adsorbant, silica, to retain hindered monoaromatics. Prior to separation of the Cerro Negro neutrals, several silicas of differing nominal pore size and from different vendors were evaluated. Smaller pore size silicas, such as the 60 Å material used here, clearly outperformed wide pore silicas due to their greater surface area per unit weight. Without reverting to special fluorocarbon eluents (141), which are prohibitively expensive for preparative scale separations, it is doubtful that the saturate/neutral-aromatic separation could be improved significantly over that obtained here.

Cerro Negro saturates are predominantly cyclic, as indicated by the inspection analyses in chapter 1, NMR and GC/MS analyses (134), and even by the D 2786 MS analysis. However, except for average structural parameters calculated from NMR, little additional information on their detailed composition and/or structures exists. The D 2786 results for ring-number distributions are suspect because the determined concentrations for both zero-ring saturates and monoaromatics have already been shown to be inaccurate by independent methods. Application of field ionization MS, or an analogous method, would be required to significantly improve the knowledge of their composition.

Distribution of Nitrogen-Containing Compounds

Elemental nitrogen distribution was discussed earlier in conjunction with table 9. As pointed out there, all three fractions--acids, bases, and neutrals--contained significant proportions of the total nitrogen in a given boiling range. Obviously, if the ABN separation was successful, nitrogen should be present in distinctly different forms in each fraction. Since nitrogen was quantitatively recovered in the saturate/neutral-aromatic separation and since the saturates contained essentially no nitrogen, the distribution of nitrogen types in neutral versus neutral-aromatic fractions was assumed to be equivalent. Furthermore, the relative concentration of nitrogen compounds in neutrals versus neutral-aromatics on a whole fraction basis was interconverted simply by accounting for the dilution effect from saturates in the whole neutrals.

The concentration of compounds containing an N-H functionality in each fraction was determined by infrared (IR) spectroscopy. As figure 8 shows, all three fractions from the 425-550° C distillate, as well as the whole distillate itself, exhibited N-H bands in the IR. Corresponding spectra in other distillate ranges were similar. Taken at face value, this result indicates a mediocre separation. However, the N-H moiety exists in a wide variety of known compounds, including amines, pyrrolic benzologs, amides, azoles, oximes, and other classes.

Table 14 lists wavenumbers of maximum absorbance ($\tilde{\nu}_{\max}$) and molar absorptivities at $\tilde{\nu}_{\max}$ for selected members of three N-H classes previously identified in petroleum or petroleum products: aromatic amines (basic), pyrrolic benzologs (acidic), and amides (acidic/basic). No distinctly "neutral" N-H compounds are known; thus, the neutral fraction could contain sterically hindered members of the above classes, for example. Although the pyrrolic benzologs exhibit $\tilde{\nu}_{\max}$'s closest to those observed for the Cerro Negro fractions, none of the N-H types may be discounted on the basis of $\tilde{\nu}_{\max}$ alone. The significant tail of the N-H band toward lower wavenumbers in the case of base concentrates (see figure 8) is more consistent with other classes of N-H compounds.

TABLE 14. - IR characteristics of selected compounds exhibiting N-H stretching bands¹

Compound	N-H $\tilde{\nu}_{\max}$ (cm^{-1})	Molar absorptivity ($\text{Lm}^{-1} \text{mm}^{-1}$)
A. Aminoaromatics		
2,3-dimethylaniline ²	3480	3.9
	3400	4.7
indoline	3405	5.0
1,2,3,4-tetrahydroquinoline	3435	5.0
diphenylamine	3420	8.2
B. Benzologs of pyrrole		
2,4-dimethyl-3-ethylpyrrole ³	3495	14.6
2,3,4,5-tetraphenylpyrrole ³	3465	14.7
indole	3465	19.1
2,5-dimethylindole	3460	16.9
1,2,3,4-tetrahydrocarbazole	3460	18.1
carbazole	3455	17.7
benzo[a]carbazole	3460	12.8
13H-dibenzo[a,i]carbazole ³	3480	11.8
C. Amides		
benzamide ²	3510	9.4
	3405	11.6
benzanilide	3430	5.4
5-methyl-2-pyrrolidinone	3415	10.5
2-piperidone	3410	6.6
oxindole	3425	12.5
benz[c,d]indol-2-(1H)-one	3435	13.4
3,4-dihydro-2-quinolone	3398	10.1
1-isoquinolone	3400	9.4
2-quinolone	3380	4.9

¹IR spectra were obtained on dilute 1,2-dichloroethane solutions unless specified otherwise.

²Two N-H bands.

³Dichloromethane solvent, $\tilde{\nu}_{\max}$ would be ca. 20 cm^{-1} lower in 1,2-dichloroethane.

FIGURE 8. - Infrared spectra of 425-550° C ABN fractions and whole distillate. Concentrations (mg/mL) in 1,2-dichloroethane were: whole distillate - 107, acids - 19.1, bases - 23.7, and neutrals - 102. Note that many of the IR bands present in all spectra; e.g., C-H, are identified on only one spectrum. Solvent versus solvent baselines are shown in all spectra.

Although significant variation in molar absorptivity both within a given class and between classes occurred, quantities of N-H compounds were nevertheless estimated for the purpose of making rough comparisons of relative levels in the various fractions. 1,2,3,4-Tetrahydrocarbazole was arbitrarily selected as the standard for calibration. Its response was representative of that of indoles and carbazoles, which exhibited the most intense absorbance of the compounds shown in table 14. The resulting data, shown in table 15, are probably equal to or less than the actual concentrations. Data for the 200-425° C distillate were not included in table 15, because low levels of N-H compounds in all fractions prevented IR estimation. Similarly, poorly defined N-H bands observed for many of the >700° C acid and base fractions led to their exclusion from the table. In general, higher degrees of hydrogen bonding, greater compositional complexity, and related factors resulted in less distinct IR spectra for higher boiling range fractions. For example, figure 9 contrasts spectra of the whole distillate/residue with that of the neutral fraction for the 550-700° C and >700° C boiling ranges. Clearly, although the spectra for higher boiling neutrals are comparable with the 425-550° C neutrals in figure 8, the degree of resolution in spectra for the whole distillate/residue decreases drastically with increasing boiling point.

TABLE 15. - Concentrations of N-H compounds in selected fractions determined by IR¹

Boiling range (°C)	Fraction	Wt. %, N		Ratio of N-H to total N (%)	W _y ³		FY ³ (N-H)
		as N-H	total ²		as N-H	Total N ⁴	
425-550	Whole distillate	0.16	0.34	47	4.4	9.4	100
	Acids	0.92	1.25	74	25	34	40
	Bases	0.34	3.09	11	10	88	9
	Neutrals	0.072	0.14	51	2.0	3.9	40
	ABN-balance	0.14	0.34	--	--	--	89
550-770	Whole distillate	0.13	0.50	26	4.4	17	100
	Acids	0.64	1.55	48	22	45	60
	Bases	0.20	2.22	9	7.6	84	16
	Neutrals	0.061	0.17	36	2.0	5.7	37
	ABN-balance	0.15	0.52	--	--	--	113
>700	Whole residue	0.088	1.16	8	6.3	83	100
	Neutrals	0.079	0.33	24	5.3	22	28

¹ 1,2,3,4-Tetrahydrocarbazole was used for calibration.

² From table 8.

³ Same meaning as in tables 9-11.

⁴ From table 9.

FIGURE 9. - Infrared spectra of high boiling neutrals versus the corresponding whole distillate/residue. Concentrations (mg/mL) in 1,2-dichloroethane were: 550-700° whole distillate - 97, neutrals - 112, >700° whole residue - 100, neutrals - 112. c.f. Fig. 8. Note that many of the IR bands present in all spectra are identified on only one spectrum, and that upper trace is solvent versus solvent baseline.

The 425-550° C acids held the highest percentage of total nitrogen as N-H types (74%). The corresponding result for the 550-700° C acids was 48%. However, the reader is reminded that these results are based on the N-H response for 1,2,3,4-tetrahydrocarbazole. Had a lower molar response been assumed, e.g., 12.8 (benzo[a]carbazole) or 11.8 (13H-dibenzo[a,i]carbazole), results much nearer to 100% would have been obtained. In fact, the lower apparent percentage of N-H types in the 550-700° C versus 425-550° C acids may simply reflect the decreasing molar absorptivity observed for higher ring pyrrolic benzologs (table 14) rather than any real compositional difference. Bases clearly contain only minor amounts of N-H compounds, ca. 10% of the total nitrogen compounds present. However, it should be noted that had an aminoaromatic or selected amides been used for calibration, N-H concentrations two to three times higher would have been calculated. Perhaps the most surprising results were for neutrals. First, up to 50% (425-550°) of the neutral nitrogen was of N-H type. Second, this percentage apparently decreased with boiling point, although this effect could be due to variation in response factors, as discussed above for acids. Third, 30-40% of the total N-H compounds in a given boiling range (see Fy results) occurred in the neutral fraction. Thus, although the presence of different N-H classes in acid versus base fractions could be rationalized, the infrared data strongly suggested overlap of one or more N-H types into the neutral fraction.

High resolution MS analysis indicated significant differences in nitrogen compound distribution over ABN fractions, however. For example, figures 10 and 11 show "Z-series" distributions for nitrogen compounds in ABN fractions from the 200-425° C and 425-550° C distillates, respectively.

FIGURE 10. - Z-series distributions of nitrogen ($C_nH_{2n+2}N$) compounds in 200-425° C acid, base, and neutral-aromatic concentrates. Results are expressed on a weight percent distillate basis.

FIGURE 11. - Z-series distributions of nitrogen ($C_nH_{2n+2}N$) compounds in 425-550°C acid, base, and neutral-aromatic concentrates. Results are expressed on a weight percent distillate basis.

The Z-series terminology is derived from the empirical formulas of a given homologous series. In the case of single nitrogen compounds, all species may be defined by the general formula: $C_nH_{2n+Z}N$. Thus, Z expresses the number of hydrogens present ($2n+Z$) for a given carbon number "n." As illustrated in figure 12(A), this manner of designating a series of alkyl homologs is particularly convenient because the value of Z does not change with an increasing number of carbons in alkyl chains. However, the Z-value does not define structure--only empirical formula. The latter concept is demonstrated in figure 12(B), where three very different structures possessing identical formulas and therefore Z-values are given. Finally, as shown in figure 12(C), the mathematical effect on Z of adding a fused benzene ring to a given structure is to decrease it by 6 (pyrrole: $Z = -3$, indole: $Z = -9$, carbazole: $Z = -15$, etc.), the corresponding decrease from addition of a cycloalkyl ring is -2 (carbazole: $Z = -15$, tetrahydrobenzo[a]carbazole: $Z = -17$), and addition of a phenyl substituent decreases Z by 8 (carbazole: $Z = -15$, phenylcarbazole: $Z = -23$).

With the above background information, the maxima in Z-series distributions for acid fractions in figures 10 and 11 may now be readily explained; maxima occurring at $Z = -15$, -21 , and -27 correspond to alkylcarbazoles, alkylbenzocarbazoles, and alkyl dibenzocarbazoles, respectively (see figure 12(C)). Cycloalkyl- and phenyl-substituted forms, while definitely present, are not as abundant as the parent compounds. Thus, the lack of corresponding maxima in distributions for nitrogen compounds in base and neutral fractions is therefore quite significant and clearly indicates distinct differences in distributions of aromatic types between acid versus neutral or base concentrates. The latter finding stands out in particular against the IR results, which indicated similar N-H/total N ratios for acids and neutrals, and a much lower ratio for bases.

<u>A</u>				
Formula	C_5H_5N	$C_8H_{11}N$	$C_8H_{11}N$	$C_{15}H_{25}N$
Z	-5	-5	-5	-5
Structure

<u>B</u>			
Type	Acidic	Basic	Very Weakly Acidic
Formula	$C_{18}H_{21}N$	$C_{18}H_{21}N$	$C_{18}H_{21}N$
Z	-15	-15	-15
Structure

<u>C</u>				
Name	Pyrrole	Indole	Carbazole	Tetrahydrobenzo[a]carbazole
Z	-3	-9	-15	-17
Structure
Name	Benzo[a]carbazole	13 H-Dibenzo[a,i]carbazole	1-phenylcarbazole	
Z	-21	-27	-23	
Structure

FIGURE 12. - Illustration of the Z-series concept. (A) $Z = -5$ for all alkylpyridines regardless of carbon number or number of substituents. (B) Examples of the wide variation in structure possible for a given empirical formula: $C_{18}H_{21}N$ ($Z = -15$). (C) Z-values of representative pyrrolic benzologs. See text.

An alternate approach in presenting the MS data is to plot carbon number distributions (i.e., value of n in $C_nH_{2n+Z}N$) for a given Z number. Example plots for $Z = -15$ and -21 are shown in figures 13 and 14 for 200–425° C, and 425–550° C fractions, respectively. Once again, the results for acid fractions differ significantly from those for bases/neutrals. In the case of acids, distinct maxima were observed for both alkylcarbazoles (figure 13) and benzocarbazoles (figure 14) at carbon numbers corresponding to C_4H_9 -substituted homologs in each case. Moreover, distributions for these species in Athabasca bitumen are quite similar to those for Cerro Negro (44,121). The broad carbon number and Z -series distributions for base and neutral nitrogen compounds again imply significantly different structures from those encountered in acid fractions.

Reconciliation of the IR versus MS results leads to the following conclusions: 1) Although acid and neutral fractions contain similar percentages of total N as N-H types, their aromatic ring and carbon number distributions are quite different. 2) The possibility that N-H types in neutrals are predominantly highly alkylated, i.e., sterically hindered, compounds of the same types present in acid fractions is refuted by the dissimilarity in the Z -series distributions for the two fractions. 3) A predominance of N-alkylated pyrrolic benzologs in the neutral fraction appears unlikely because of the significant percentage of the total N in neutrals as N-H types and the lack of maxima in Z -series distributions corresponding to those observed for acids. 4) If any overlap of similar N-H types occurred, it was probably between neutrals and bases.

As mentioned above, the occurrence of N-H types and qualitative appearance of the IR band for base fractions suggested the presence of amines. However, this class is more typical of upgraded, especially hydrotreated, streams than raw crudes. Nevertheless, this possibility was examined using nonaqueous titration techniques.

FIGURE 13. - Carbon number distribution for $C_{12}H_{2n-15}N$ compounds in 200-425° C acid, base, and neutral-aromatic concentrates. Results are expressed on a weight percent distillate basis.

FIGURE 14. - Carbon number distribution for $C_{10}H_{20-21}N$ compounds in 425-550° C acid, base, and neutral-aromatic concentrates. Results are expressed on a weight percent distillate basis.

The approach employed involves titration of separate aliquots of a given base fraction in two different solvents, acetonitrile and acetic anhydride. In the former, azaaromatics (benzologs of pyridine) and arylamines cotitrate in the first equivalence point. Occasionally, selected weaker bases titrate in a second equivalence point, but typically only one equivalence point is observed with titration in acetonitrile. If alkylamines are present, they titrate prior to azaaromatics plus arylamines, thus giving rise to a total of three theoretical equivalence points. In acetic anhydride, all amines acylate to form amides, which titrate along with other weak bases in the last equivalence point. Therefore, the presence and quantity of aromatic versus aliphatic amines may be deduced from the differential titration behavior in the two solvents. The method is based on the work of Buell (142); further details appear elsewhere (140), and in chapter 4.

Table 16 shows results from titration of both base and acid fractions using the above approach. Acid fractions were titrated in the same manner as bases to determine if they contained any basic or amphoteric types. Results shown for bases are averages from three or more titrations; data for acids represent a single determination in most cases. Titrations typically exhibit relative repeatabilities of $\pm 5\%$, but precision is somewhat sample dependent. The results clearly indicate the absence of detectable amounts of aliphatic or aromatic amines in any of the base fractions. In fact, the difference between the acetonitrile and first acetic anhydride endpoints ($EP_{ACN} - EP_{AA1}$) was typically slightly negative, owing to the cotitration of a small amount of other base types with azaaromatics in the first acetic anhydride equivalence point.

TABLE 16. - Results from nonaqueous titration with perchloric acid

Boiling range (°C)	Fraction	EP ¹ _{ACN}	EP ² _{AA1}	EP ² _{AA2}	EP _{ACN} -EP ³ _{AA1}	EP _{AA1} +EP _{AA2}	HNP ⁴ _{ACN}	HPN _{AA1}	HPN _{AA2}	Azaaromatics	Weak bases	Nontitratable bases	% Total acids titrating as bases
		-----meq HClO ₄ /g-----					-----mv-----			-----mole %-----			
200-425	Base	1.89	1.91	0.89	-0.02	2.80	240	225	550	57	27	16	--
425-550	Base	1.27	1.34	0.98	-0.07	2.32	250	220	595	51	42	7	--
	Acid	0.13	0.28	ND ⁵	-0.15	0.28	200	380	ND	--	--	--	11
550-700	Base	0.79	0.82	1.00	-0.03	1.82	250	230	595	42	54	4	--
	Acid	0.09	0.34	ND	-0.25	0.34	230	375	ND	--	--	--	16
>700	Strong base	0.38	0.37	0.42	0.01	0.79	260	230	490	42	46	12	--
	Weak base I	0.08	0.09	0.42	-0.01	0.51	340	250	450	10 ⁶	53	37	--
	Strong acid	0.10	0.16	ND	-0.06	0.16	295	420	ND	--	--	--	14
	Weak acid I	0.14	0.17	ND	-0.03	0.17	310	420	ND	--	--	--	16

¹ Endpoint in acetonitrile solvent.

² First and second endpoints in acetic anhydride solvents are designated AA1 and AA2, respectively.

³ A positive value for the difference indicates presence of arylamines.

⁴ HNP = half neutralization potential, which is analogous to pKa in aqueous systems. A lower HNP denotes stronger basicity.

⁵ None detected.

⁶ HNP_{ACN} was above the normal range for azaaromatics.

Acetonitrile results (EP_{ACN}) were used in conjunction with average molecular weights in chapter 1 to calculate the percent azaaromatics in each base fraction. Obviously, the results carry the assumption that only this class contributed to EP_{ACN} . Similarly, EP_{AA2} was used to calculate total weak bases. Finally, the difference between azaaromatics plus weak bases and 100% was expressed as nontitratable bases. These calculations indicate a declining azaaromatic content, relative to total bases, with increasing boiling point and a corresponding increase in weak bases. It should be remembered, however, that total base yield increases rapidly with boiling point (table 7); therefore, both azaaromatics and weak bases are actually increasing on a whole distillate basis, but the latter are increasing at a faster rate. Nontitratable bases--which would include ketones, pyrrolic benzologs, and many other classes potentially present--are a relatively minor percentage except in the case of the $>700^{\circ}C$ weak base-I fraction. Although the $>700^{\circ}C$ weak base-II fraction was not titrated, its nontitratable base content would have been greater than or equal to the result for the weak base-I fraction in all probability.

The observed increase in weak bases with boiling range and, in the case of $>700^{\circ}C$ bases, increases in nontitratable bases are natural consequences of the increasing number of heteroatoms per molecule discussed earlier in conjunction with tables 9-11. For example, addition of O, S, and even N to a given base as a substituent or via its insertion into the aromatic nucleus almost always lowers its basicity (143). Furthermore, basicity decreases with increasing aromaticity; e.g., pyridine is a stronger base than quinoline (143). Thus, even without the occurrence of additional heteroatoms, the basicity of a given class typically decreases with boiling point due to increasing size of aromatic nuclei in higher boiling fractions. In addition, the probability of titration of two basic groups in the same molecule is quite low, because their net interaction lowers each group's basicity and because formation of dicationic salts in nonaqueous media is inherently unfavorable. The net effect of the above factors is to broaden the effective HNP range for a given basic class, and generally introduce some ambiguity into interpretation of the titration results for high-boiling fractions.

**DO NOT MICROFILM
THIS PAGE**

CHAPTER 3

Titration of acids with perchloric acid revealed the presence of a fairly constant, ca. 15%, degree of basic functionality. It is not known whether this represents amphoteric/bifunctional species, which would logically be contained in acid fractions since acids were separated before bases, or contamination by bases. However, this fairly significant level of basic functionality may indicate that the IR results for the fraction of total nitrogen as N-H types may be more accurate than implied by the preceding discussion.

Table 17 summarizes quantitative group type results from high resolution MS analysis of the 200-425° C and 425-550° C base fractions. The raw MS results indicate that 98% of bases in either fraction contain nitrogen, a result significantly higher than the maximum possible based on elemental N data (table 9). This apparent discrepancy probably resulted from either lack of ionization or detection of molecular ions for relatively saturated SO-, SO₂-, and/or O_x-containing species. This situation definitely occurred for acids (see below) where essentially none of the carboxylic acids were detected in the MS analysis. Furthermore, the low apparent H/C ratios, the low oxygen content, and the high nitrogen levels calculated from MS data compared to combustion data (table 8) further support this contention. Therefore, the MS results were normalized to a total nitrogen content in agreement with the corresponding combustion data, and the balance was reported simply as "unidentified material."

Figures 15 and 16 show Z-series distributions for major nitrogen-containing compound types in 200-425° C and 425-550° C bases, respectively. Maxima in the distributions for NS-compounds at Z = -15 and -21 in both figures suggest azadibenzothiophene and azabenzonaphthothiophene structures, respectively, as prominent NS species. The corresponding distributions for NO-compounds are relatively smooth, which is more consistent with amide types than azafuran benzologs which would be expected to show maxima corresponding to those for NS-compounds. Thiophene and furan are the sulfur and oxygen analogs of pyrrole (figure 12), respectively, and their presence in a given structure would be expected to produce maxima in Z-series distributions corresponding to those observed for pyrrolic benzologs in acid fractions (see figs. 10 and 11).

FIGURE 15. - Z-series distributions of nitrogen (N), nitrogen-sulfur (NS) and nitrogen-oxygen (NO) compounds in 200-425° C bases. Results are expressed on a weight percent of concentrate basis.

FIGURE 16. - Z-series distributions of nitrogen (N), nitrogen-sulfur (NS) and nitrogen-oxygen (NO) compounds in 425-550° C bases. Results are expressed on a weight percent of concentrate basis.

TABLE 17. - Composition of Cerro Negro 200-425° C and 425-550° C base concentrates (wt %) from mass spectrometric analysis

Compound Type	Raw Data		Corrected Data ¹	
	200-425° C	425-550° C	200-425° C	425-550° C
N-compounds	60.4	54.7	53	48
NS-compounds	26.6	25.7	23	23
NS ₂ -compounds	2.1	2.5	1.8	2.2
NS ₃ -compounds	-	0.1	-	0.1
NO-compounds	7.4	10.5	6.4	9.2
NOS-compounds	0.9	3.6	0.8	3.2
NOS ₂ -compounds	-	0.2	-	0.2
Hydrocarbons	0.5	0.5	0.4	0.4
S-compounds	2.0	1.0	1.7	0.9
S ₂ -compounds	-	0.2	-	0.2
N ₂ -compounds	0.1	1.2	0.1	0.9
N ₂ S-compounds	0.1	-	0.1	-
Unidentified ²	-	-	13	12
Average Molecular Weight	289	400	-	-
Calculated Elemental Composition				
C	81.4	83.8	79.85 ³	82.91 ³
H	9.1	9.0	9.69	9.66
H/C ⁴	1.33	1.28	1.446	1.388
N	4.7	3.5	4.05	3.09
O	0.5	0.3	3.09	1.33
S	4.3	3.5	2.75	3.05

¹See text.

²Probably saturated compounds containing oxygen.

³Actual elemental composition from table 8.

⁴Atomic ratio.

Correlation of IR, titration, elemental, and MS results for bases showed good agreement between MS results for N-compounds and azaaromatics determined by titration (tables 16 and 17). In addition, the IR estimate for N-H types in the 425-550° C bases (10%, table 15) was in good agreement with the corresponding MS result for NO-compounds (9.2%, table 17), which suggests the presence of amides. The calculated concentration of carbonyl compounds in 425-550° C bases, based on the intensity of the IR band at 1695 cm⁻¹ (see figure 8) and an assumed molar absorptivity of 55 L m⁻¹ mm⁻¹, was 13 wt %.

This result is well within experimental error of the corresponding IR estimate for N-H types and the MS result for NO-compounds. Comparison of the sum of MS types containing sulfur with the total sulfur-containing species predicted from elemental sulfur content (table 10) showed reasonable agreement in the case of 200-425° C (29% versus 26%, respectively), and 425-550° C bases (33% versus 38%, respectively). The levels of nontitratable bases greatly exceeded MS-determined concentrations of hydrocarbons and sulfur compounds, thereby indicating the presence of types other than neutral contaminants which did not titrate. Correlation of the titration parameter "weak bases" with results from the other techniques was difficult because of its vagueness. However, most or all of the NS-compounds determined from MS analysis almost certainly fell into the weak base category. For example, the sum of NS- plus NS₂-compounds (25%) for 200-425° C bases nearly accounted for weak bases determined by titration (27%). However, in the case of 425-550° C bases, total weak bases (42%) exceeded total NS_x-compounds (25%) significantly. Thus, other types shown in table 17, including NO-compounds, probably contributed to weak bases in that boiling range. The weaker basicity of NS- or NO-types compared to N-types such as azaaromatics is consistent with the known effect of additional heteroatoms toward decreasing basicity, as discussed earlier.

In summary, the application of elemental, infrared, nonaqueous titration and MS techniques toward determination of the nitrogen compound distributions in ABN fractions yielded some useful results and conclusions. However, since each technique measures different parameters which cannot generally be interrelated, the end result fell far short of a definitive analysis. The conclusions which were drawn are summarized and categorized below for the benefit of the reader.

Highly probable:

- Nitrogen compounds in acid fractions are primarily pyrrolic benzologs.
- Basic nitrogen compounds consist of the following types:
azaaromatics, including NS analogs, and to a lesser degree of certainty, amides. Neither aliphatic nor aromatic amines are present in significant amounts.

- A significant percentage of neutral nitrogen compounds is of N-H type, potentially with pyrrole-based structures. However, their aromaticity, as reflected in Z-series distributions, and carbon number distributions are completely dissimilar to the species in acid fractions.

Probable:

- The concentration of pyrrolic benzologs in distillate acid fractions may be reliably estimated from their elemental nitrogen content.
- Nonaqueous titration in acetonitrile provides an accurate measure of azaaromatics in base fractions.
- Base fractions contain minor amounts of relatively saturated oxygen- and/or SO_x -containing species.
- N-alkylated pyrrolic benzologs corresponding to those found in acid fractions do not comprise a significant proportion of nitrogen compounds in neutral fractions.

Speculative:

- The structure shown in figure 12(B), far right, is a reasonable representation of nitrogen compounds in the neutral fraction.

From the standpoint of the objective of isolation of minor classes from the bulk oil matrix, the occurrence of any nitrogen compounds in the neutral fraction should be viewed as a disadvantage. Thus, a secondary objective of the sulfide separation method, discussed in chapter 5B, was further removal of nitrogen compounds from neutrals. However, the bulk of the neutral nitrogen compounds passed through both the silica precolumn and the various metal-loaded columns investigated for sulfide isolation. This observation alone indicates both their very weak polarity and the infeasibility of improving the nonaqueous ion exchange procedure to the point where all nitrogen compounds partition into acid or base fractions.

The FeCl_3 -clay procedure developed during the USBM-API 60 project did not achieve the goal of complete nitrogen removal either. As discussed in the

Introduction, the total yield of acids + bases + neutral nitrogen compounds obtained from Wilmington distillates in their work was nearly identical to the sum of acids and bases obtained with the optimized ABN procedure alone. Snyder, et al. (32) also reported difficulties in isolation and identification of nitrogen compounds exhibiting low degrees of polarity. Thus, this is not a new separation problem.

On the other hand, the current ABN procedure does allow for differentiation of acidic versus basic versus neutral nitrogen types. Furthermore, had the fully optimized nonaqueous ion exchange method been employed throughout the work on Cerro Negro, the concentration of nitrogen in neutral fractions would undoubtedly have been lower. The latter contention is supported by the lower total N and N-H content of neutrals obtained from 1-propanol versus methanol washed-resins (11) and by the corresponding increase in the proportion of N-H types in acid concentrates obtained from the optimized procedure (see chapter 3). The recent ABN results obtained on Cerro Negro 425-550° C and >700° C boiling ranges also support increased recovery of "neutral" nitrogen into acid fractions using the optimized procedure (see Appendix 2).

One interesting aspect of "neutral" nitrogen compounds is their apparent resistance to hydrodenitrogenation or, alternately, formation from other nitrogen-containing species. For example, separation and analysis of acids in a straight-run Wilmington gas oil compared to several hydrotreated products indicated greatest survival (or formation) of nitrogen compounds exhibiting acidities weaker than "normal" pyrrolic benzologs (144). Z-series and carbon number distributions for those weakly acidic species were similar to those shown here for neutral nitrogen compounds in Cerro Negro 200-425° C and 425-550° C distillates. In addition, the relative proportion of total nitrogen in neutral fractions increased with hydrotreating severity for both Wilmington and Mayan (Mexican crude) gas oils (Appendix 3). Since Cerro Negro heavy distillates will almost certainly require hydrotreating, further work on separation and analysis of neutral nitrogen compounds seems justified, especially since these compounds appear to be prevalent in other heavy crudes as well.

Given the limitations in the available analysis techniques, the best option available for obtaining more definitive information on nitrogen compound distributions over ABN fractions was to reduce their complexity through additional separations. The latter decision led to work described in chapters 3-5.

Distribution of Oxygen-Containing Compounds

The previously discussed lack of reliable elemental oxygen data constitutes a significant disadvantage in the determination of types and concentrations of oxygen-containing compounds in ABN fractions. Furthermore, whole acid fractions are poorly suited for direct high resolution MS analysis because the carboxylic acids exhibit poor molecular ion sensitivities, poor ionization efficiencies due to their largely saturated hydrocarbon skeletons, and potentially, decarboxylation to hydrocarbons and/or adsorption on the heated glass inlet surface. As the result, MS data for whole acids are not quantitative for any type, since results for aromatic species were too high and results for carboxylic acids too low. However, in spite of these difficulties, some useful data were obtained.

Levels of carboxyl, hydroxyl, and, as discussed earlier, N-H-compounds in acid fractions, were determined from IR spectra. Also, since the HPLC method for subfractionating acids (chapter 3) yielded reasonably pure carboxylic acid concentrates, their mass recoveries were used to crosscheck IR results. IR response for carboxylic acids was determined from measurements on actual Cerro Negro subfractions in addition to pure compounds. Since the main difficulty in IR analysis was generally the selection of appropriate response factors, use of actual fractions for calibration enabled a much higher degree of accuracy in IR results than was possible from calibration with pure compounds alone. Nonaqueous titration was employed as the third independent method for assessing carboxylic acid concentrations. Because they are significantly more acidic than the bulk of the other acid types, carboxylic acids titrate at a separate equivalence point from the weaker acids. Since hydroxyl compounds give an inherently mediocre IR response, which is further complicated by hydrogen bonding effects and interference from water, they were also determined after conversion to trifluoroacetates in selected cases. Finally, the relative ratio of hydroxyl/carboxyl functional groups in 425-550° C acids

was also measured with ^{119}Sn NMR after reaction with bis(tri-*n*-butyltin) oxide (TBT0) during evaluation of a method published by Rafii, et al. (145). Detailed discussion of all these methods is deferred until chapter 3, but representative spectra and titration curves are shown here to facilitate understanding of the results.

The IR spectrum of 425–550° C acids shown in figure 8 (page 61) is representative of all distillate acid fractions. As indicated in the figure, discernible bands for O-H, N-H, and carboxylic acids were observed. Its poor sensitivity, resolution, and positive interference by water cause the O-H band to be a mediocre indicator of hydroxyl content. However, approximate correction for the contribution of the water band at 3600 cm^{-1} to total hydroxyl absorbance at 3590 cm^{-1} can be made by measuring the resolved free water band at 3690 cm^{-1} and dividing its intensity by 2.4. The approximate 2.4:1 intensity ratio of the two water bands is evident in the spectrum for the 425–550° C bases, which do not contain hydroxyl compounds, and was confirmed from the spectrum of pure water in 1,2-dichloromethane. The O-H band at 3590 cm^{-1} does not include a contribution from free carboxylic acid O-H, which absorbs at ca. 3470 cm^{-1} . The latter band does interfere with the N-H band (3460 cm^{-1}), however. This latter interference is generally not severe due to the low molar absorptivity of the carboxylic O-H band and because at least half of the carboxylic acids typically exist as hydrogen-bonded dimers. The dimerization phenomenon is responsible for the characteristic dual carbonyl adsorption for carboxylic acids, with monomeric species absorbing near 1750 cm^{-1} and dimers at ca. 1710 cm^{-1} . The hydrogen-bonded carboxylic acid O-H gives rise to the very broad band covering the region from 3300 cm^{-1} to 2500 cm^{-1} . Hydrogen-bonded water also contributes to this region.

IR spectra of whole distillates clearly indicated the same bands as found in the whole acids, and the spectra of neutrals and bases did not show detectable quantities of either hydroxyl compounds or carboxylic acids (see figures 8 and 9). Thus, to the extent of the limited sensitivity for the IR technique, clean partitioning of those types into the acid fraction occurred. Given the previously demonstrated ability of the anion resin to retain pyrrolic benzologs, which are generally weaker acids than hydroxyaromatics and weaker than carboxylic acids by several orders of

classes into the acid fraction is hardly surprising. However, during the evaluation of extraction methods discussed in the Introduction, incomplete recovery of even carboxylic acids into the acid fraction was frequently observed, especially for high-boiling materials.

In order to overcome the many deficiencies of direct IR analysis of whole acids, a chemical derivatization procedure was developed which converts hydroxyl compounds to trifluoroacetate esters and carboxylic acids to esters of 2,2,2-trifluoroethanol. The IR spectrum of the derivatized acids is markedly different than that of the underivatized material, as demonstrated in figure 17. In the case of the plain acids, the free hydroxyl band is not even visible at the relatively dilute concentration shown, and the N-H band is completely masked by the carboxyl O-H band at 3470 cm^{-1} . Thus, the only measurable species are carboxylic acids. However, after derivatization, the N-H band and bands corresponding to the derivatives are clearly visible. Partial acylation of the N-H compounds typically occurs, yielding a shoulder or small band at 1720 cm^{-1} for the corresponding amides. Thus, neither the free N-H band nor the band for the trifluoroacetamides is useful for quantitating N-H types after derivatization with the current version of the method. Preliminary results from the derivatization approach applied to $>700^\circ\text{C}$ acids are also encouraging, as indicated in figure 18. In that case, only the acylation reaction was performed, but the resulting trifluoroacetate ester band was clearly discernible. The free O-H band was not detectable in the spectrum of the underivatized $>700^\circ\text{C}$ strong acids.

Carboxylic acid content was also determined by nonaqueous titration. Figure 19 compares titration curves of a simple two-component mixture versus $200\text{--}425^\circ\text{C}$ acids. The titrant employed, potassium dimsyl, has sufficient basicity for neutralization of even very weak acids such as 1,2,3,4-tetrahydrocarbazole. The mole percent of carboxylic acids is computed from the ratio of the first equivalent point versus the sum of both equivalence points.

FIGURE 17. - IR spectra of plain versus derivatized 200-425° C acids.

FIGURE 18. - IR spectra of plain versus acylated $>700^\circ\text{C}$ strong acids. Concentrations were 10.0 and 15.7 mg/mL dichloromethane, respectively.

FIGURE 19. - Titration curves of benzoic acid plus 1,2,3,4-tetrahydrocarbazole (A) and Cerro Negro 200-425° C whole acids (B). Equivalence points for carboxylic and weak acids are designated "1" and "2", respectively.

Figure 20 shows the ^{119}Sn NMR spectrum of TBT0-derivatized 425-550° C acids. Peaks for derivatives of hydroxyl compounds and carboxylic acids are well resolved. Although the peak from the excess TBT0 overlaps with that of the carboxylic acids somewhat, its effect on quantitation of carboxylic acids was usually minimal. Integration of the indicated peaks yielded relative areas for hydroxyl- and carboxyl-derivatives of 22% and 79%, respectively. In this case and in general, quantitative results obtained with this method disagreed significantly with those from other methods, both on Cerro Negro fractions as well as those from other crudes. This approach was ultimately abandoned in favor of a ^{13}C methylation procedure, which is currently undergoing evaluation.

Table 18 summarizes results for acidic classes from the various methods. Results for pyrrolic benzologs are repeated from earlier tables to facilitate comparison with those of the oxygen-containing compounds. Although the detailed discussion of each method's relative merits and limitations shall be deferred until chapter 3, the overall agreement between results from different methods actually exceeded expectations. However, two sets of results, carboxylic acid content via IR measurement of 2,2,2-trifluoroesters and direct IR determination of pyrrolic benzologs, were in substantial disagreement with those from other methods. The reason for the apparently low data from IR measurements of 2,2,2-trifluoroesters is not presently understood; the problems in selecting the appropriate IR calibration factor for determination of N-H were discussed in the previous section.

The results show decreasing relative proportions of both carboxylic acids and hydroxyl compounds in higher boiling acid fractions. However, as pointed out earlier in connection with basic compound class distributions, the significant increase in total acid content with boiling point more than compensates for the effect of the relative decreases on an acid fraction basis, thereby giving net increases for both types on a whole distillate/residue basis. By the same token, the apparent increase in pyrrolic benzologs on an acid fraction basis is even more dramatic on a whole distillate basis. This class is notorious for its undesirable effects on refining behavior and product properties. For example, pyrrolic benzologs undergo hydrodenitrogenation at significantly slower rates than basic nitrogen types (118,141).

FIGURE 20. - ^{119}Sn NMR spectrum of bis-(tri-*n*-butyltin) oxide (TBTO) derivatized 425-550° C acids. imp = impurity in the TBTO reagent. SB = side band of TBTO produced from coupling of ^{119}Sn with ^{13}C in *n*-butyl substituents.

Although somewhat simplistic, the three general classes listed in table 18 accounted for ca. 90% of all distillable acids. Even though analytical difficulties largely precluded obtaining comparable data for the $>700^{\circ}\text{C}$ acids, except for carboxylic acids, it is doubtful that this approach would have been meaningful for that boiling range anyway--given the number of heteroatoms per molecule predicted from elemental analysis (see discussion, p. 52). Even for distillable acids, the complexity of heteroatomic types indicated by high resolution MS was much greater than implied by IR or the other methods listed in the table (see below).

Table 19 shows raw and corrected high resolution MS results for compound types in the $200\text{--}425^{\circ}\text{C}$ and $425\text{--}550^{\circ}\text{C}$ acids. From comparison of the raw total of concentrations of all types which could possibly contain carboxylic groups ($\text{O}_2\text{--}$, $\text{O}_2\text{S--}$, $\text{O}_2\text{S}_2\text{--}$ and $\text{O}_2\text{N--}$ compounds) with the average results for carboxylic acids in table 18, it became obvious that a major correction of the raw data in table 19 would be necessary to obtain even reasonable agreement with data in table 18. As explained earlier, the reason for this discrepancy was the unsuitability of the MS sample introduction mode (heated batch inlet) and ionization method (nominal 10 eV electron impact) for analysis of carboxylic acids. Thus, the raw data were corrected as follows: the sum of the N, NS, NS_2 , NO, NOS, N_2 , O, OS, S, and in the case of $425\text{--}550^{\circ}\text{C}$ acids only, hydrocarbons were divided into (100 minus the wt % carboxylic acids from table 18); then, that ratio (0.64 for $200\text{--}425^{\circ}\text{C}$, 0.60 for $425\text{--}550^{\circ}\text{C}$) was used to correct the raw result for each compound type except $\text{O}_2\text{--}$ compounds. The latter was calculated by difference. Since the $200\text{--}425^{\circ}\text{C}$ result for hydrocarbons was totally inconsistent with carryover from neutrals, especially considering that the result for S-compounds was only 0.7% (the $200\text{--}425^{\circ}\text{C}$ neutral-aromatics contain 40% sulfur compounds, see table 10), those species were excluded from the normalization factor for that boiling range, and their corrected concentration was arbitrarily set to zero. The hydrocarbons observed in the analysis of the $200\text{--}425^{\circ}\text{C}$ fraction probably represented decarboxylated species or fragment ions. This may have also been the case for the $425\text{--}550^{\circ}\text{C}$ fraction, but, due to the small concentration observed, they were included in the normalization factor. Obviously, had significant quantities of thiols or other acidic S-compounds been present, assignment of the $200\text{--}425^{\circ}\text{C}$ hydrocarbon ions as artifact species would not have been as clearcut, because the resulting higher levels of S-compounds could have been misinterpreted as neutral contaminants.

TABLE 18. - Results for compound class distributions in acid fractions determined by different methods

Boiling Range, (°C)	Method ¹	Carboxylic Acids	Hydroxyl Compounds	Pyrrolic Benzologs	Total
200-425	IR	64±2 ²	9.7	16	-
	IR (Der.)	55	10.0±0.1	-	-
	HPLC	63±2	-	-	-
	NAT	62±1	-	-	-
	Elemental	- ⁴	-	14	-
	Average ³	63	9.9	14	87
425-550	IR	58±2	6.7	25±1	-
	IR (Der.)	51±1	6.8±0.1	-	-
	HPLC	56±1	6.5±0.5	34±4	-
	NAT	56±1	-	-	-
	Elemental	-	-	34	-
	Average	57	6.7	34	98
550-700	IR	36±2	5.4	22±1	-
	HPLC	36	-	-	-
	NAT	43±1	-	-	-
	Elemental	-	-	45	-
	Average	38	5.4	45	88
>700 Strong	HPLC	15	-	-	-
	NAT	11±2	-	-	-
	Average	14	-	-	-
Weak-I	NAT	ND ⁵	-	-	-
Weak-II	NAT	ND ⁵	-	-	-

¹IR = plain IR, IR (Der.) - IR with acylation/esterification. HPLC = HPLC subfraction yields from chapter 3. NAT = nonaqueous titration. Elemental = calculation from elemental N content (table 9).

²In cases where multiple determinations were made with a given method, standard deviation of replicates are included with the mean.

³IR (Der.) results were not included in the mean for carboxylic acids. Also, IR results for pyrrolic benzologs were excluded in the mean for that class.

⁴A dash indicates no determination.

⁵ND = None detected.

TABLE 19. - Composition of Cerro Negro 200-425° C and 425-550° C acid concentrates (wt %) from mass spectrometric analysis

Compound Type	Raw Data		Corrected Data ¹	
	200-425° C	425-550° C	200-425° C	425-550° C
N-compounds	36.1	41.0	23	25
NS-compounds	1.7	8.7	1.1	5.2
NS ₂ -compounds	-	0.5	-	0.3
NO-compounds	1.7	5.5	1.1	3.3
NOS-compounds	0.1	1.2	-	0.7
N ₂ -compounds	-	0.4	-	0.2
O-compounds	14.9	6.1	9.6	3.7
OS-compounds	2.5	5.3	1.6	3.2
O ₂ -compounds	12.3	12.3	55	47
O ₂ S-compounds	12.5	14.5	8.0	8.7
O ₂ S ₂ -compounds	-	1.2	-	0.7
O ₂ N-compounds	-	0.7	-	0.4
Hydrocarbons	10.9	1.4	-	0.8
S-compounds	0.7	1.2	0.4	0.7
Average molecular wt.	250	341	-	-
Calculated elemental composition				
C	82.6	83.7	78.60 ³	79.09 ³
H	8.7	7.9	9.88	9.60
H/C ²	1.25	1.12	1.498	1.447
N	2.4	2.6	0.66	1.25
O	4.3	3.1	8.84	6.21
S	2.0	2.8	1.36	2.43

¹See text.

²Atomic ratio.

³Actual elemental composition from table 8.

Reconciliation of the corrected MS data with results for hydroxyl and pyrrolic compounds in table 18 revealed much improved agreement compared to the raw data. For example, the corrected totals for nitrogen-containing species for the 200-425° C and 425-550° C fractions from MS were 25 and 35%, respectively, compared to 14 and 34% in table 18. Comparable agreement was obtained between MS data for O- plus OS-compounds versus total hydroxyl compounds in table 18 as well. Although it is recognized that even the corrected data in table 18 may be inaccurate, they surely represent an improvement over the raw data.

Putting problems with quantitation aside, the most striking features of the MS analysis were both the variety of types detected and the surprisingly high levels of types containing three and even four heteroatoms. As explained earlier, this situation was anticipated for $>700^{\circ}\text{C}$ acid fractions based on elemental data, but not for distillable acids. Three or four heteroatom-species were also detected during MS analysis of bases (table 17), but only at trace levels. Nevertheless, based on the simplicity of the IR spectra and corroboration of quantitative IR data with results from independent methods, the bulk of the distillable acids still must contain only one acidic functional group and, furthermore, the bulk of the acidic groups must be carboxylic--with the balance consisting of mostly O-H and N-H functionalities. The dearth of single sulfur types detected by MS coupled with the absence of a detectable S-H band in the IR discounts the possibility of significant levels of thiol groups. Thus, the bulk of the sulfur is probably in thiophenic or sulfide structures. However, the perchloric acid titration results (table 16) for acid fractions suggest significant percentages of N, SO, NO, or other heteroatom combinations in basic configurations. With the available data, the structures of types listed in table 19 cannot be defined beyond the above generalizations. Moreover, corresponding data for the $550\text{--}700^{\circ}\text{C}$ and $>700^{\circ}\text{C}$ fractions would probably exhibit a much greater number of types. For these reasons, further separation of whole acids into subtypes would definitely be required to obtain a more definitive breakdown of acidic classes and structures.

As discussed in the nitrogen-compound section, the major oxygen-containing class in base fractions was tentatively identified as amides, and the existence of other unidentified oxygen-containing classes was inferred from circumstantial evidence. The apparent molar ratio of carbonyl versus N-H bands in the IR spectra of bases was typically greater than one and increased with boiling range to two or more for the $>700^{\circ}\text{C}$ base fractions. This increasing ratio can be accounted for in many ways, however, including variation in molar response for each band. Thus, evidence for basic carbonyl types other than amides is inconclusive. IR spectra of bases also exhibited minor bands consistent with SO and SO₂ types. For example, correspondence in wavenumbers for bands in $425\text{--}550^{\circ}\text{C}$ bases (CCl₄ solution)--1290, 1130, and 1075 cm^{-1} --was reasonably close to SO₂ and SO bands of pure compounds obtained from CCl₄ solution; e.g., dibenzothiophene sulfone (1290 and 1160 cm^{-1}) and

dimethyl sulfoxide (1070 cm^{-1}). No SO or SO₂ types were detected in the MS analysis of base fractions (table 17), but minor amounts of NOS and NOS₂ were found. Even though the latter types could potentially have contributed to the SO band in the IR, the most probable explanation is that SO and SO₂ types were undetected in the MS analysis, and therefore comprise part of the estimated 13 and 12 percent of unidentified material in the 200-425° C and 425-550° C bases, respectively (table 17). Thus, the bulk of the accountable basic oxygen appears to be in amide and sulfoxide/sulfone forms.

Neutral oxygen types could potentially include alcoholic, ether, or selected carbonyl functionalities. Although small carbonyl bands were typically evident in IR spectra of neutral fractions (see figures 8 and 9), Z-series distributions from MS analysis of 200-425° C and 425-550° C neutral-aromatic fractions indicated that the bulk of neutral oxygen was present as benzologs of furan. For example, figures 21 and 22 compare Z-series distributions for single oxygen compounds in ABN fractions for 200-425° C and 425-550° C boiling ranges, respectively. Acidic C_nH_{2n+2}O species exhibited rather featureless Z-series distributions, consistent with a broad range of hydroxylated aromatic structures. However, the corresponding distributions for neutral-aromatic fractions were quite reminiscent of those observed for pyrrolic nitrogen compounds in acid fractions. Since furan is the oxygen analog of pyrrole, the close correspondence in their Z-series distributions suggests parallel structures for those types in their respective fractions. Maxima evident in figures 21 and 22 at Z = -16, -22, and -28 correspond to alkyl dibenzofurans and structures with one and two additional fused aromatic rings, respectively. As shown earlier in table 17, no single O-compounds or O_x-types were detected in the MS analysis of bases. However, as discussed earlier, it is possible that saturated O_x-compounds or O_x-species with other structural features which similarly prevented ionization and/or detection by MS may have been present as part of the "unidentified" material listed in the table.

FIGURE 21. - Z-series distribution of oxygen ($C_nH_{2n+2}O$) compounds in 200-425° C acid, base, and neutral-aromatic concentrates. Results are expressed on a weight percent distillate basis. No single oxygen compounds were detected in the base concentrate.

FIGURE 22. - Z-series distribution of oxygen ($C_nH_{2n+2}O$) compounds in 425-550° C acid, base, and neutral-aromatic concentrates. Results are expressed on a weight percent distillate basis. No single oxygen compounds were detected in the base concentrate.

Although the current set of results on oxygen compound distributions is not extensive enough to serve as a basis for recalculating elemental oxygen-based parameters shown earlier in table 11, it can be used to pinpoint those data most likely to be in error. For example, the weight percents of compounds containing oxygen in each fraction (Wy) appear reasonable in the case of acid and neutral/neutral-aromatic fractions, but much higher for base fractions than justifiable on the basis of identified basic compound classes. Since the results calculated for levels of 200-425° C and 425-550° C oxygen-containing bases, 58 and 33%, respectively (table 11), greatly exceed the total oxygen types determined by MS analysis (table 17), it is suggested that much of the error in the ABN balances for oxygen versus those determined for whole distillates (table 8) was due to erroneously high elemental oxygen results for base concentrates, at least in the case of the 200-425° C and 425-550° C boiling ranges. If that is indeed the case, then yet another possibility for the "unidentified" bases in table 17 is some type of oxygen-rich contaminant. Since IR and Karl Fisher estimates for water content of base fractions do not account for the high apparent oxygen levels by themselves, the presence of additional oxygen in organic species is implied. Oxidation of neutral sulfur-containing species to sulfoxides or sulfones during the ABN separation and subsequent isolation of those species in base fractions is consistent with high elemental oxygen balances and the MS and IR results for base fractions. Presence of an oxygen-rich solvent impurity is also a possibility. Finally, misassignment of empirical formulas during interpretation of the MS data and/or variations in MS sensitivities may also have contributed to the discrepancy between MS-calculated versus actual oxygen contents. Specifically, ions assumed to represent nitrogen compound fragments could conceivably have been molecular ions from O₃-compounds; since the exact masses of the two types are nearly identical in selected series, definitive assignment was not possible. Given the abundance of nitrogen compounds, however, their assignment as fragment ions appeared to be the most plausible. Of the above, oxidation of neutral sulfur types to sulfones/sulfoxides is the explanation for the cited discrepancies which best fits the available data.

In spite of the analytical difficulties in tracking oxygen distributions, the following conclusions appear justified:

- The bulk of the oxygen present in distillates occurs in acidic functional groups (predominantly carboxylic acids).

- Neutral forms of oxygen comprise roughly one-third of the total oxygen present in distillates. The bulk of the neutral oxygen compounds are benzologs of furan.
- Only minor amounts of oxygen appear in basic structures in the unaltered crude.
- The ABN separation effectively partitions the major oxygen types into the anticipated fraction with minimal overlap.

Distributions of Hydrocarbons and Sulfur-containing Compounds

Results presented in previous sections (tables 17 and 19) have indicated very low levels of hydrocarbons and neutral sulfur compounds in acid and base fractions. Thus, at least in the case of 200-425° C and 425-550° C distillates, minimal carryover of neutrals into polar fractions occurred. The fact that sulfur almost invariably occurs only in structures containing other heteroatoms for both acid and base fractions strongly suggests that it is largely incorporated into the hydrocarbon skeletons rather than the functional groups. The sole exception appears to be basic SO- and SO₂-compounds which, as discussed above, may be formed via oxidation of neutral sulfur compounds during separation and/or fraction workup.

As expected, hydrocarbons and sulfur compounds are the dominant types in neutral-aromatic fractions. Table 20 summarizes results from MS analysis of neutral-aromatics from the 200-425 and 425-550° C boiling ranges. The relative agreement between MS-calculated and combustion results for elemental composition for neutral-aromatic fractions was significantly better than for either acid or base fractions. Thus, no correction of the raw MS results was necessary. As the result of the agreement in elemental data, close correspondence between levels of neutral compound types calculated from elemental results (tables 9-11) versus those determined by MS was also observed, especially given the approximations employed in calculating the data in tables 9-11.

Figures 23 and 24 show Z-series distributions for the three major types--hydrocarbons, S-, and S₂-compounds--in the 200-425° C and 425-550° C neutral-aromatic fractions, respectively.

Important aspects of neutral-aromatic composition evident in the figures are outlined below:

FIGURE 23. - Z-series distributions of hydrocarbons (H), sulfur compounds (S), and disulfur compounds (S₂) in 200-425° C neutral-aromatics concentrate. Results are expressed on a wt % of concentrate basis.

FIGURE 24. - Z-series distributions of hydrocarbons (H), sulfur compounds (S), and disulfur compounds (S₂) in 425-550° C neutral-aromatics concentrate. Results are expressed on a wt % of concentrate basis.

- Aromatic hydrocarbons in the 200-425° C distillates largely range from monoaromatics ($Z = -6$) to compounds containing up to four aromatic rings ($Z = -24$). Small amounts of lower Z-series compounds ($Z > -6$) detected may represent contamination by saturates or, more likely, were actually mass spectral fragment ions. Small amounts of more condensed ($Z < -24$) aromatic hydrocarbons probably boil above 425° C and thus represent material present as the result of overlap from the distillation.

TABLE 20. - Composition of the Cerro Negro 200-425° C and 425-550° C neutral-aromatic concentrates (wt %) from mass spectrometric analysis

Compound type	200-425° C	425-550° C
Aromatic hydrocarbons	55.6	35.3
S-compounds	37.4	45.2
S ₂ -compounds	1.3	11.4
S ₃ -compounds	-	0.2
Furan types and other O-compounds	2.0	1.3
SO-compounds	0.8	0.6
O ₂ -compounds	0.1	0.1
N-compounds	0.5	5.7
NS-compounds	-	1.3
NS ₂ -compounds	-	0.1
NO-compounds	-	trace
Average molecular weight	263	396
Calculated elemental composition ¹		
C	85.5 (84.38)	84.6 (84.28)
H	9.3 (10.37)	9.5 (10.42)
H/C ²	1.30 (1.465)	1.34 (1.473)
N	0.02 (0.048)	0.2 (0.18)
O	0.14 (0.14)	0.1 (0.15)
S	5.0 (4.90)	5.6 (4.79)

¹Data in parenthesis are combustion results from table 8.

²Atomic ratio.

- Aromatic hydrocarbons in the 425-550° C distillate largely range from cycloalkylmonoaromatics ($Z = -8$) to compounds containing five or possibly six aromatic rings ($Z = -32$). Small amounts of lower and higher Z -series compounds arise from the same factors explained above for the 200-425° C hydrocarbons.
- Dominant Z -series for aromatic hydrocarbons in the 200-425° C distillate ranged from $Z = -10$ to $Z = -18$. For the 425-550° C distillate, the most intense series ranged from $Z = -16$ to $Z = -22$. These results suggest a predominance of compounds containing two to three aromatic rings in the lower distillate and three to four aromatic rings in the higher distillate.
- As discussed previously for pyrrolic benzologs in acid fractions and furanic benzologs in neutral-aromatics, the maxima observed in Z -series distributions for S -compounds are most consistent with a predominance of thiophenic sulfur types, since thiophene is the corresponding sulfur analog of pyrrole and furan. Thus, the Z -series distribution for monosulfur compounds in the 200-425° C distillates implies predominately benzothiophenes ($-10S$) and dibenzothiophenes ($-16S$). The $-12S$ and $-14S$ types are probably mono- and dicycloalkyl-benzothiophenes, respectively. Higher series ($-18S$, $-20S$, and $-22S$) probably represent cycloalkyl-, dicycloalkyl-, and benzo- forms of dibenzothiophene, respectively.
- The much smoother Z -series distribution for 425-550° C neutral-aromatic monosulfur compounds results from a higher percentage of total sulfur present as sulfides as well as greater complexity of thiophenic types than in the 200-425° C neutral-aromatics. Since the sulfide functionality can exist in any type of alkylaromatic or saturated structure, that type would be expected to exhibit smooth Z -series distributions. Sulfide content of neutral-aromatic fractions was independently determined by a ligand exchange LC procedure described in chapter 5B. Those results are reprinted here in table 21 for convenient reference. As the table shows, sulfide content increased from 10.6 to 23.1 wt % over the 200-425° C to 425-550° C

neutral-aromatic fractions, respectively. Thus, comparison of data in tables 20 and 21 indicates a significantly higher relative contribution of sulfides to total sulfur types for 425-550° C neutral-aromatics which accounts for their smoother Z-series distribution.

- Disulfur types were minor in the 200-425° C neutral-aromatics but much more prevalent in those boiling between 425-550° C. Probably, at least one sulfur is of thiophenic type in most compounds. This conclusion is based on the predominance of thiophenic sulfur forms over sulfides indicated by results from more extensive separation and analysis of neutral-aromatic fractions (chapter 5B), and by the appearance of maxima in the S₂ Z-series distributions in both figures.

TABLE 21. - Mass balances from sulfides separations (wt %)¹

Boiling Range, ° C	Nonsulfides	Sulfides	Polars	Total Recovered
<u>A. Whole neutral basis</u>				
200-425	88.28	6.26	2.09	96.63
425-550	77.88	17.61	3.90	99.39
550-700	71.12	22.77	6.23	100.12
700+	44.86	40.15	18.90	103.91
<u>B. Neutral-aromatic fraction basis</u>				
200-425	85.9	10.6	3.5	100
425-550	71.8	23.1	5.1	100
550-700	66.5	26.3	7.2	100
700+	38.1	42.1	19.8	100
<u>C. Whole distillate/residue basis</u>				
200-425	83.4	5.9	2.0	91.3
425-550	69.5	15.7	3.5	88.7
550-700	55.5	17.8	4.9	78.2
700+	14.1	12.6	6.0	32.7

¹From chapter 5B.

The above discussion of the sulfide results illustrates how additional separations can clarify apparent ambiguities in analytical data for complex fractions. In addition, the availability of those fractions represents a significant opportunity for characterization of a type commonly present in

crude oils, but for which little detailed structural information exists because of interference from thiophenic types during analysis of whole neutral-aromatic fractions. Similarly, analysis of sulfide-free neutral-aromatics would yield data for thiophenic types without sulfide interference.

CONCLUDING REMARKS

To a large extent, progress in development and verification of chemical separation methods for petroleum is limited by methodology for analysis of the fractions rather than separation theory and practice. This generalization certainly applies to the present work, especially in the case of the ABN method. In terms of practical applications and basic data such as elemental and mass balances, the methods described here are significantly ahead of many of those reviewed in the introductory section. However, in terms of detailed knowledge of the partitioning of specific classes and structures, many of the reviewed methods are better understood and verified. Obviously, one of the objectives of work in subsequent chapters is to improve this level of understanding for the current methods.

The compositional complexity of Cerro Negro crude is overwhelming. Because of the time required in analysis of fractions, this oil is actually a poor choice for use in development of separation methods. Thus, here and in later chapters, other petroleums and synthetic fuels were employed for much of the developmental work; the application to Cerro Negro was reserved for the "ultimate test" of the procedure.

A major challenge exists in devising effective methods for presenting the compositional data for this crude, without oversimplifying it to the point where it conveys no more information than simple inspection properties. For example, a listing of the complete carbon number and Z-series distributions for the 200-425° C neutral-aromatic fractions, the simplest fraction discussed here, required 15 pages in another report (133). Expansion of that presentation to include a breakdown of multiple structural types and classes possible for each homolog would have lengthened it significantly. Thus, a complete listing of the **available** data for ABN fractions from even the 200-425° C distillate would have at least doubled the length of this report. While this quantity of data was judged to be well outside the scope of this report, the more relevant question is: is it outside the scope of human

comprehension? The latter question leads to many follow-up ones, including why the additional work in later chapters was done in an effort to further refine (i.e., add to) the results obtained here. The best justifications are: 1) development of the methods was the key objective throughout the project, 2) many practical production and refining problems persist because the shortcomings in present analysis methods prevent identification of the species responsible for the problem (e.g., corrosion, well plugging, and product stability), and 3) the current problems are expected to magnify as it becomes necessary to utilize heavier crudes. Finally, the reader is referred back to statements in the last paragraph of the Foreword section which further discuss overall objectives and justification of the work.

Two of the largest potential drawbacks to the ABN method are 1) relatively high background levels of ion exchange on resin-derived impurities contaminating the resulting fractions and 2) the significant levels of nitrogen compounds remaining in the neutral fractions. Current work toward refinement of the method is aimed at resolving or at least minimizing these problems. Perhaps the ABN procedure's greatest strength is its ability to produce fractions from virtually any type of material. Work continues toward enhancing its versatility, wherever possible. On the other hand, the saturate/neutral-aromatic procedure is a relatively mature method, which has undergone little change in recent years.

REFERENCES

1. Miller, J. M. Separation Methods in Chemical Analysis, J. Wiley, New York, NY, 1975.
2. Snyder, L. R. Principles of Adsorption Chromatography, M. Dekker, New York, NY, 1968.
3. Snyder, L. R., and J. J. Kirkland. Introduction to Modern Liquid Chromatography, 2nd Ed., J. Wiley, New York, NY, 1979.
4. Boduszynski, M. M. Chemistry of Asphaltenes, Adv. Chem. Series No. 195, J. W. Bunger and N. C. Li (Eds.), Amer. Chem. Soc., Wash., DC, 1981, Chapter 7.
5. Selucky, M. L., S. S. Kim, F. Skinner, and O. P. Strausz. Chemistry of Asphaltenes, Adv. Chem. Series No. 195, J. W. Bunger and N. C. Li (Eds.), Amer. Chem. Soc., Wash., DC, 1981, Chapter 6.
6. Long, R. B. Chemistry of Asphaltenes, Adv. Chem. Series No. 195, J. W. Bunger and N. C. Li (Eds.), Amer. Chem. Soc., Wash., DC, 1981, Chapter 2.
7. Smith, P.A.S., J. C. Romine and S. P. Chou. Amer. Chem. Soc., Div. Petrol. Chem. Prepr., v. 24, 1979, p. 974.
8. Martin, T. G., C. A. Smith, C. E. Snape, and H. C. Starkie. Fuel, v. 60, 1981, p. 365.
9. Wallace, S., M. J. Crook, K. D. Bartle, and A. J. Pappin. Fuel, v. 65, 1986, p. 138.
10. Finseth, D. H., Z. T. Przybylski, and C. E. Schmidl. Fuel, v. 61, 1982, p. 1174.
11. Green, J. B., R. J. Hoff, P. W. Woodward, and L. L. Stevens. Fuel, v. 63, 1984, p. 1290.
12. Dooley, J. E., W. C. Lanning, and C. J. Thomson. Refining of Synthetic Crudes, Adv. Chem. Series 179, M. L. Gorbaty and B. M. Harney (Eds.), Amer. Chem. Soc., Wash., DC, 1979.
13. Buchanan, M. V. Anal. Chem., v. 56, 1984, p. 546.
14. Ho, C.-H., C. Y. Ma, B. R. Clark, M. R. Guerin, T. K. Rao, and J. L. Epler. Environ. Res., v. 22, 1980, p. 412.
15. Katoh, T., and K. Ouchi. Fuel, v. 66, 1987, p. 1588.
16. Smith, P.A.S., J. C. Romine, S. S. P. Chou, and R. P. Schroder. Chemistry of Asphaltenes, J. W. Bunger and N. C. Li (Eds.), Adv. Chem. Ser. No. 195, Am. Chem. Soc., Wash., DC, 1981, Chapter 9.

17. Ijam, M. J., R. S. Al-Ameeri, M. A. Fahim, and S. F. Aref. Amer. Chem. Soc., Div. Petrol. Chem. Prepr., v. 31, 1986, p. 256.
18. Natusch, D. F. S., and B. A. Tomkins. Anal. Chem., v. 50, 1978, p. 1429.
19. Fruchter, J. S., J. C. Laul, M. R. Petersen, P. W. Ryan, and M. E. Turner. Analytical Chemistry of Liquid Fuel Sources, P. C. Uden, S. Siggia, and H. B. Jensen (Eds.), Adv. Chem. Ser. No. 170, Am. Chem. Soc., Wash., DC, 1978, Chapter 18.
20. Fish, R. H., and J. J. Komlenic. Anal. Chem., v. 56, 1984, p. 510.
21. Fish, R. H., J. J. Komlenic, and B. K. Wines. Anal. Chem., v. 56, 1984, p. 2452.
22. Wehner, H., and M. Teschner. J. Chromatogr., v. 204, 1981, p. 481.
23. Wallace, D., D. Henry, K. Pongar, and D. Zimmerman. Fuel, v. 66, 1987, p. 44.
24. Suatoni, J. C., and R. E. Swab. J. Chromatogr. Sci., v. 14, 1976, p. 535.
25. Radke, M., H. Willsch, and D. H. Welte. Anal. Chem., v. 52, 1980, p. 406.
26. Dark, W. A. J. Liq. Chromatogr., v. 5, 1982, p. 1645.
27. Grizzle, P. L., and D. M. Sablotny. Anal. Chem., v. 58, 1986, p. 2389.
28. Bollet, C., J. C. Escalier, C. Souteyrand, M. Caude, and J. Rossett. J. Chromatogr., v. 206, 1981, p. 289.
29. Miller, R. Anal. Chem., v. 54, 1982, p. 1742.
30. Pearson, C. D., and S. G. Gharfeh. Anal. Chem., v. 58, 1986, p. 307.
31. Jewell, D. M., E. W. Albaugh, B. E. Davis, and R. G. Ruberto. Ind. Eng. Chem. Fundam., v. 13, 1974, p. 278.
32. Snyder, L. R., B. E. Buell, H. E. Howard. Anal. Chem., v. 40, 1968, p. 1303.
33. Snyder, L. R. Anal. Chem., v. 41, 1969, p. 1084.
34. Snyder, L. R. Acc. Chem. Res., v. 3, 1970, p. 290.
35. McKay, J. F., T. E. Cogswell, J. H. Weber, and D. R. Latham. Fuel, v. 54, 1975, p. 50.
36. McKay, J. F., J. H. Weber, and D. R. Latham. Anal. Chem., v. 48, 1976, p. 891.

37. McKay, J. F., P. J. Amend, P. M. Harnsberger, T. E. Cogswell, and D. R. Latham. *Fuel*, v. 60, 1981, p. 14.
38. McKay, J. F., P. M. Harnsberger, R. B. Erickson, T. E. Cogswell, and D. R. Latham. *Fuel*, v. 60, 1981, p. 17.
39. McKay, J. F., D. R. Latham, and W. E. Haines. *Fuel*, v. 60, 1981, p. 27.
40. Snyder, L. R., and D. L. Saunders. *Chromatography in Petroleum Analysis*, K. H. Altgelt and T. H. Gouw (Eds.), M. Dekker, New York, NY, 1979, Chapter 10.
41. Bunger, J. W., K. P. Thomas, and S. M. Dorrence. *Fuel*, v. 58, 1979, p. 183.
42. Payzant, J. D., A. M. Hogg, D. S. Montgomery, and O. P. Strausz. *AOSTRA J. Res.*, v. 1, 1985, p. 175.
43. Payzant, J. D., A. M. Hogg, D. S. Montgomery, and O. P. Strausz. *AOSTRA J. Res.*, v. 1, 1985, p. 183.
44. Payzant, J. D., A. M. Hogg, D. S. Montgomery, and O. P. Strausz. *AOSTRA J. Res.*, v. 1, 1985, p. 203.
45. Holmes, S. A. *AOSTRA J. Res.*, v. 2, 1986, p. 167.
46. Rall, H. T., C. J. Thomson, H. J. Coleman, and R. L. Hopkins. *Sulfur Compounds in Crude Oil*, U.S. Dept. Interior Bur. Mines Bull. No. 659, 1972.
47. Farcasiu, M. *Fuel*, v. 56, 1977, p. 9.
48. Odoerfer, G. A., L. R. Rudnik, and D. D. Whitehurst. *Amer. Chem. Soc., Div. Fuel Chem. Prepr.*, v. 26, No. 2, 1981, p. 89.
49. Whitehurst, D. D., S. E. Buttrill, F. J. Derbyshire, M. Farcasiu, G. A. Odoerfer, and L. R. Rudnick. *Fuel*, v. 61, 1982, p. 994.
50. Seshadri, K. S., and D. C. Cronauer. *Fuel*, v. 62, 1983, p. 1436.
51. Seshadri, K. S., D. C. Young, and D. C. Cronauer. *Fuel*, v. 64, 1985, p. 22.
52. Jacobs, F. S., and R. H. Filby. *Fuel*, v. 62, 1983, p. 1186.
53. Cronauer, D. C., D. C. Young, J. Solash, K. S. Seshadri, and D. A. Danner. *Ind. Eng. Chem. Process Des. Dev.*, v. 25, 1986, p. 756.
54. Nomura, A., M. Yazaemon, and Y. Kogure. *Bull. Chem. Soc. Japan*, v. 52, 1979, p. 817.
55. Schiller, J. E., and D. R. Mathiason. *Anal. Chem.*, v. 49, 1977, p. 1225.

56. Callen, R. B., J. G. Bendoraitis, C. A. Simpson, and S. E. Voltz. *Ind. Eng. Chem. Prod. Res. Dev.*, v. 15, 1976, p. 222.
57. Callen, R. B., C. A. Simpson, and J. G. Bendoraitis. *Analytical Chemistry of Liquid Fuel Sources*, P. C. Uden, S. Siggia, and H. B. Jensen (Eds.), *Adv. Chem. Ser. No. 170*, Am. Chem. Soc., Wash., DC, 1978, Chapter 21.
58. Holmes, S. A., and K. A. Raska. *Fuel*, v. 65, 1986, p. 1539.
59. Green, J. B., B. K. Stierwalt, J. S. Thomson, and C. A. Treese. *Anal. Chem.*, v. 57, 1985, p. 2207.
60. Gould, K. A., and R. B. Long. *Fuel*, v. 65, 1986, p. 572.
61. Green, J. B., and P. L. Grizzle. *Trace Analysis*, v. 2, J. F. Lawrence (Ed.), Academic P., New York, NY, 1982, pp. 223-265.
62. Ruckmick, S. C., and R. J. Hurtubise. *J. Chromatogr.*, v. 321, 1985, p. 343.
63. Matsunaga, A., and S. Kusayanagi. *Amer. Chem. Soc., Div. Fuel Chem. Prepr.*, v. 26, No. 2, 1981, p. 59.
64. Matsunaga, A. *Anal. Chem.*, v. 55, 1983, p. 1375.
65. Altgelt, K. H., D. R. Latham, D. M. Jewell, and M. L. Selucky. *Chromatography in Petroleum Analysis*, K. H. Altgelt and T. H. Gouw (Eds.), M. Dekker, New York, NY, 1979, Chapter 9.
66. Jewell, D. M., J. H. Weber, J. W. Bunger, H. Plancher, and D. R. Latham. *Anal. Chem.*, v. 44, 1972, p. 1391.
67. Hirsch, D. E., R. L. Hopkins, H. J. Coleman, F. O. Cotton, and C. J. Thompson. *Anal. Chem.*, v. 44, 1972, p. 915.
68. Coleman, H. J., J. E. Dooley, D. E. Hirsch, and C. J. Thompson. *Anal. Chem.*, v. 45, 1973, p. 1724.
69. Dooley, J. E., D. E. Hirsch, C. J. Thompson, and C. C. Ward. *Hydroc. Process.*, v. 53, No. 11, 1974, p. 187.
70. Cogswell, T. E., J. F. McKay, and D. R. Latham. *Anal. Chem.*, v. 43, 1971, p. 1766.
71. McKay, J. F., D. M. Jewell, and D. R. Latham. *Separation Sci.*, v. 7, 1972, p. 361.
72. Hirsch, D. E., H. J. Coleman, J. E. Dooley, and C. J. Thompson. *Developing Empirical Correlations from Basic GPC Data and Deriving of Fundamental GPC Parameters for a Given System*. ERDA-BERC/RI-76/14, 1977, 66 pp.

73. Bunger, J. W. Shale Oil, Tar Sands, and Related Fuel Sources, T. F. Yen (Ed.), Adv. Chem. Ser. No. 151, Am. Chem. Soc., Wash., DC, 1976, Chapter 10.
74. McKay, J. F., P. J. Amend, T. E. Cogswell, P. M. Harnsberger, R. B. Erickson, and D. R. Latham. Analytical Chemistry of Liquid Fuel Sources, P. C. Uden, S. Siggia, and H. B. Jensen (Eds.), Adv. Chem. Ser. No. 170, Am. Chem. Soc., Wash., DC, 1978, Chapter 9.
75. Selucky, M. L., T. C. S. Ruo, Y. Chu, and O. P. Strausz. Analytical Chemistry of Liquid Fuel Sources, P. C. Uden, S. Siggia, and H. B. Jensen (Eds.), Adv. Chem. Ser. No. 170, Am. Chem. Soc., Wash., DC, 1978, Chapter 8.
76. Selucky, M. L., Y. Chu, T. C. S. Ruo, and O. P. Strausz. Fuel, v. 56, 1977, p. 369.
77. Selucky, M. L., Y. Chu, T. C. S. Ruo, and O. P. Strausz. Fuel, v. 57, 1978, p. 9.
78. Sawatzky, H., S. M. Ahmed, A. E. George, and G. T. Smiley. Am. Chem. Soc., Div. Petrol. Chem. Prepr., v. 23, 1978, p. 11.
79. Petrakis, L., R. G. Ruberto, D. C. Young, and B. C. Gates. Ind. Eng. Chem. Process. Des. Dev., v. 22, 1983, p. 292 and 298.
80. McKay, J. F., M. M. Boduszynski, and D. R. Latham. Liq. Fuels Technol., v. 1, 1983, p. 35.
81. McKay, J. F., and S.-L. Chong. Liq. Fuels Technol., v. 1, 1983, p. 289.
82. Young, L.-J. S., T. Hara, and N. C. Li. Fuel, v. 63, 1984, p. 816.
83. Arzel, T., S. G. Colgrove, L. W. Dennis, and S. D. Reynolds. Am. Chem. Soc., Div. Fuel Chem. Prepr., v. 30, No. 4, 1985, p. 122.
84. Desbene, P. L., D. Richard, D. Lambert, J. J. Basselier, R. Boulet, and A. Y. Hue. Analusis, v. 14, 1986, p. 148.
85. Snyder, L. R. Anal. Chem., v. 41, 1969, p. 315.
86. Snyder, L. R., and B. E. Buell. Anal. Chem., v. 40, 1968, p. 1295.
87. Later, D. W., M. L. Lee, K. D. Bartle, R. C. Kong, and D. L. Vassilaros. Anal. Chem., v. 53, 1981, p. 1612.
88. Later, D. W., T. G. Anders, M. L. Lee. Anal. Chem., v. 55, 1983, p. 2126.
89. Later, D. W., B. W. Wilson, and M. L. Lee. Anal. Chem., v. 57, 1985, p. 2979.
90. Nishioka, M., R. M. Campbell, M. L. Lee, and R. N. Castle. Fuel, v. 65, 1986, p. 270.

91. Later, D. W., R. B. Lucke, E. K. Chess, and J. A. Franz. *Fuel*, v. 66, 1987, p. 1347.
92. Borra, C., D. Wiesler, and M. Novotny. *Anal. Chem.*, v. 59, 1987, p. 339.
93. Andersson, J. T. *Anal. Chem.*, v. 59, 1987, p. 2207.
94. Andreolini, F., C. Borra, D. Wiesler, and M. Novotny. *J. Chromatogr.*, v. 406, 1987, p. 375.
95. Rubin, I. B., M. R. Guerin, A. A. Hardigree, and J. L. Epler. *Environ. Res.*, v. 12, 1976, p. 358.
96. Jones, A. R., M. R. Guerin, and B. R. Clark. *Anal. Chem.*, v. 49, 1977, p. 1766.
97. Guerin, M. R., I. B. Rubin, T. K. Rao, B. R. Clark, and J. L. Epler. *Fuel*, v. 60, 1981, p. 282.
98. Buchanan, M. V. *Anal. Chem.*, v. 54, 1982, p. 570.
99. Tomkins, B. A., and C.-H. Ho. *Anal. Chem.*, v. 54, 1982, p. 91.
100. Boduszynski, M. M., R. J. Hurtubise, and H. F. Silver. *Anal. Chem.*, v. 54, 1982, p. 372.
101. Boduszynski, M. M., R. J. Hurtubise, and H. F. Silver. *Anal. Chem.*, v. 54, p. 375.
102. Boduszynski, M. M., R. J. Hurtubise, T. W. Allen, and H. F. Silver. *Anal. Chem.*, v. 55, 1983, p. 225.
103. Boduszynski, M. M., R. J. Hurtubise, T. W. Allen, and H. F. Silver. *Anal. Chem.*, v. 55, 1983, p. 232.
104. Boduszynski, M. M., R. J. Hurtubise, and H. F. Silver. *Fuel*, v. 63, 1984, p. 93.
105. Boduszynski, M. M., R. J. Hurtubise, T. W. Allen, and H. F. Silver. *Fuel*, v. 64, 1985, p. 242.
106. Allen, T. W., R. J. Hurtubise, and H. F. Silver. *Anal. Chem.*, v. 57, 1985, p. 666.
107. Boduszynski, M. M., R. J. Hurtubise, T. W. Allen, and H. F. Silver. *Fuel*, v. 65, 1986, p. 223.
108. Ruckmick, S. C., R. J. Hurtubise, and H. F. Silver. *Fuel*, v. 65, 1986, p. 1677.
109. Ramljak, A. Solc., P. Arpino, J.-M. Schmitter, and G. Guiochon. *Anal. Chem.*, v. 49, 1977, p. 1222.

110. Amat, M., P. Arpino, J. Orrit, A. Lattes, and G. Guiochon. *Analisis*, v. 8, No. 5, 1980, p. 179.
111. Schmitter, J.-M., P. Arpino, and G. Guiochon. *J. Chromatogr.*, v. 167, 1978, p. 149.
112. Lancas, F. M., E. M. Soares, H. S. Karam, and H. M. McNair. *Am. Chem. Soc., Div. Fuel Chem. Prepr.*, v. 30, No. 2, 1985, p. 273.
113. Schmitter, J. M., Z. Vajta, and P. J. Arpino. *Advances in Organic Geochemistry 1979*, A. G. Douglas and J. R. Maxwell (Eds.), Pergamon P., Oxford, U.K., 1980, p. 67-76.
114. Schmitter, J.-M., H. Colin, J.-L. Excoffier, P. Arpino, and G. Guiochon. *Anal. Chem.*, v. 54, 1982, p. 769.
115. Schmitter, J.-M., I. Ignatiadis, P. Arpino, and G. Guiochon. *Anal. Chem.*, v. 55, 1983, p. 1685.
116. Dorbon, M., J.-M. Schmitter, P. Arpino, and G. Guiochon. *J. Chromatogr.*, v. 246, 1982, p. 255.
117. Schmitter, J.-M., I. Ignatiadis, M. Dorbon, P. Arpino, G. Guiochon, H. Toulhoat, and A. Huc. *Fuel*, v. 63, 1984, p. 557.
118. Dorbon, M., I. Ignatiadis, J.-M. Schmitter, P. Arpino, G. Guiochon, H. Toulhoat, and A. Huc. *Fuel*, v. 63, 1984, p. 565.
119. Schmitter, J.-M., I. Ignatiadis, and P. J. Arpino. *Geochim. Cosmochim. Acta*, v. 47, 1983, p. 1975.
120. Dorbon, M., J. M. Schmitter, P. Garrigues, I. Ignatiadis, M. Ewald, P. Arpino, and G. Guiochon. *Org. Geochem.*, v. 7, 1984, p. 111.
121. Frakman, Z., T. M. Ignasiak, D. S. Montgomery, and O. P. Strausz. *AOSTRA J. Res.*, v. 3, 1987, p. 131.
122. Wise, S. A., S. N. Chesler, H. S. Hertz, L. R. Hilpert, and W. E. May. *Anal. Chem.*, v. 49, 1977, p. 2306.
123. Strachan, M. G., and R. B. Johns. *Anal. Chem.*, v. 59, 1987, p. 636.
124. Boduszynski, M. M., J. F. McKay, and D. R. Latham. *Am. Chem. Soc., Div. Petrol. Chem. Prepr.*, v. 26, 1981, p. 865.
125. Green, J. B., and R. J. Hoff. *J. Chromatogr.*, v. 209, 1981, p. 231.
126. Klimisch, H.-J., and A. Beiss. *J. Chromatogr.*, v. 128, 1976, p. 117.
127. Desbene, P. L., D. C. Lambert, P. Richardin, J.-J. Basselier, A. Y. Huc, and R. Boulet. *Anal. Chem.*, v. 56, 1984, p. 313.
128. Strachan, M. G., and R. B. Johns. *Anal. Chem.*, v. 58, 1986, p. 312.

129. Burchill, P., A. A. Herod, J. P. Mahon, and E. Pritchard. J. Chromatogr., v. 265, 1983, p. 223.
130. Prudich, M. E., D. C. Cronauer, R. F. Vogel, and J. Solash. Ind. Eng. Chem. Process Des. Dev., v. 25, 1986, p. 742.
131. Marcelin, G., D. C. Cronauer, R. F. Vogel, M. E. Prudich, and J. Solash. Ind. Eng. Chem. Process Des. Dev., v. 25, 1986, p. 747.
132. Brown, J. C., R. P. Vrana, C. A. Treese, G. P. Sturm, Jr., and R. D. Grigsby. Analysis of Saturate Fractions from Cerro Negro 200-425° C and 425-550° C Distillates. NIPER Topical Report No. 35, 1985, 87 pp.
133. Sturm, G. P., Jr., S. Y. Tang, R. D. Grigsby, D. E. Hirsch, and C. A. Treese. The Application of Mass Spectrometric Methods in the Characterization of the 200-425° C and 425-550° C Acid, Base, and Neutral-Aromatic Fractions of Cerro Negro Crude. NIPER Topical Report No. 111, 1985, 46 pp.
134. Netzel, D. A., and F. D. Guffey. NMR and GC/MS Investigation of the Saturate and Distillate Fractions from the Cerro Negro Heavy Petroleum. U.S. Dept. of Energy Rept. DOE/FE/60177-2440, 1987, 28 pp.
135. Vogh, J. W., and J. S. Thomson. Anal. Chem., v. 53, 1981, p. 1345.
136. Nondek, L., and J. Malek. J. Chromatogr., v. 155, 1978, p. 187.
137. Aczel, T., D. E. Allan, J. H. Harding, and E. A. Knipp. Anal. Chem., v. 42, 1970, p. 341.
138. Scheppele, S. E., K. C. Chung, and C. S. Hwang. Int. J. Mass Spectrom. Ion Phys., v. 49, 1983, p. 143.
139. Scheppele, S. E., Q. G. Grindstaff, R. D. Grigsby, S. R. McDonald, and C. S. Hwang. Int. J. Mass Spectrom. Ion Phys., v. 49, 1983, p. 179.
140. Green, J. B., B. K. Stierwalt, J. A. Green, and P. L. Grizzle. Fuel, v. 64, 1985, p. 1571.
141. Miller, R. L., L. S. Ettre, and N. G. Johansen. J. Chromatogr., v. 259, 1983, p. 393.
142. Buell, B. F. Anal. Chem., v. 39, 1967, p. 756.
143. Albert, A. Physical Methods in Heterocyclic Chemistry, v. 1, A. R. Katritzky (Ed.), Academic Press, New York, NY, 1963, pp. 1-108.
144. Sturm, G. P., Jr., J. B. Green, S. Y. Tang, J. W. Reynolds, and S. K.-T. Yu. Detailed Analysis of Polar Compounds in Wilmington Gas Oil and Hydrotreated Products. NIPER Topical Report No. 152, 1986, 63 pp.
145. Rafii, E., R. Faure, L. Lena, E.-J. Vincent, and J. Metzger. Anal. Chem., v. 57, 1985, p. 2854.

APPENDIX 1

**CURRENT PROCEDURES FOR THE PREPARATION OF RESINS
USED IN THE NIPER NONAQUEOUS ION EXCHANGE CHROMATOGRAPHIC PROCEDURE
(REVISED AUGUST 1988)**

CURRENT PROCEDURES FOR THE PREPARATION OF RESINS USED IN THE NIPER NONAQUEOUS ION EXCHANGE CHROMATOGRAPHIC PROCEDURE. (REVISED 8/88)

Anion Resin

The resin used for acid trapping is BioRad AG MP-1, which is an analytical grade of DOWEX MSA-1 resin. It comes as the chloride form and is a polystyrene-divinylbenzene type resin with quaternary ammonium chloride functional groups. The 100-200 mesh size is typically used.

Anion Resin Preparation Procedure

1. A volume of approximately 2.5-3 L of AG MP-1 Resin is placed into a 4000 mL fritted glass-based Buchner funnel, and if the resin has been previously used, it is washed with several solvents to remove the benzene and formic acid contained in used resin. The first wash is performed with one gallon (or 4 L) of acetone in about 5 portions, by stirring the acetone and resin together and sucking the slurry dry with vacuum, and repeating. This washing procedure is repeated with methanol (4 L), and then with about 2 gallons of deionized (D.I.) water.

The resin-filled funnel, which is now practically free of organic solvents, is placed into a 4 L filtering flask and is slowly washed by gravity flow (at a rate of about 8 L per day) with the following reagents in this order:

- A) 6x4 L of 1-2 N aqueous HCl (250 mL conc. HCl/4 L D.I. water).
- B) 4 L of D.I. water.
- C) 6x4 L of 1-2 N aqueous NaOH solution.
- D) 3x4 L of D.I. water.
- E) 6x4 L of 1:1 1-propanol/D.I. water.
- F) 6x4 L of 1-propanol.

G) The resin is transferred to a Soxhlet thimble with dimensions of 11.5 cm (I.D.) x 37 cm (length) which is then placed into the large Soxhlet apparatus fitted with a 12 L boiling flask and extracted with (1) 10 L of diethyl ether for 24 hr. and then (2) with 10 L of n-pentane for 24 hr. Both extractions are conducted under an argon atmosphere. The ether is preconditioned by adding 20 g of sodium metal dissolved in 500-600 mL

1-propanol followed by refluxing overnight under a slow argon purge to destroy any peroxide present before the actual extraction of the resin.

H) The finished resin is slurried into a bottle with cyclohexane, and stored under argon until used. After removal of resin from a bottle, the bottle is reblanketed with argon to exclude atmospheric water and CO₂.

Cation Resin

The resin used for base trapping is BioRad AG MP-50, which is an analytical grade of DOWEX MSC-1 resin. It comes as the hydrogen form and is a polystyrene-divinylbenzene type resin with sulfonic acid functional groups. The 100-200 mesh size is typically used.

Cation Resin Preparation Procedure

The AG MP-50 resin is bedded in a 4000 mL Buchner funnel and if previously used is washed free of organic solvents in the same manner as the MP-1 resin.

The solvent-free resin in the funnel is slowly washed with the following reagents in this order:

- A) 9x4 L of 1-2 N NaOH.
- B) 4 L of D.I. water.
- C) 4 L of 1:1 1-propanol containing/D.I. water 100 mL of conc. sulfuric acid.
- D) 8x4 L of 1-propanol containing 100 mL of conc. sulfuric acid and 100 mL of D.I. water.
- E) 6x4 L 1-propanol.
- F) The resin is transferred to the Soxhlet thimble, placed into the extractor, and extracted with ether, followed by n-pentane, exactly as above for the MP-1 resin.
- G) The finished resin is slurried into a bottle with cyclohexane, and stored under argon until used. After removal of resin from a bottle, the bottle is reblanketed with argon.

Ion exchange resins may be recycled as described above with results equivalent to those obtained with new resins. In the case of the anion resin, the HCl wash converts the spent resin, which is in the formate form, back to the chloride form. The resin is then converted to the hydroxide form via percolation with NaOH. Direct conversion from the formate to the hydroxide form is not successful, owing to the resin's affinity for the formate anion. HCl efficiently removes formate via its protonation to formic acid, which rapidly elutes from the resin. The subsequent washes with the various organic solvents effectively dehydrate the resin and remove organic impurities. However, the resin's polar functional groups retain remnants of coordinated polar solvent molecules, e.g., 1-propanol, even after extensive extraction with ethyl ether and pentane. The ether purification step has been found to be a useful precaution since over the course of several years many batches of ether have been found to be highly contaminated with peroxides.

The pretreatment of the spent cation resin, which is in the n-propylammonium form initially, with sodium hydroxide efficiently converts it to the sodium form. Conversion to the hydrogen form is effected during the alcoholic sulfuric acid treatments. As with the anion resin, a shortcut procedure to convert directly to the hydrogen form from the amine form is ineffective, because of the resin's affinity for the n-propylammonium cation. However, in 1 N NaOH, the amine cation reverts to the neutral amine form which is readily eluted from the resin. Organic solvent washes serve the same purposes as for the anion resin.

It is recognized that the above procedures undoubtedly could be streamlined and/or shortened somewhat. However, indiscriminate corner cutting will in all probability result in resins with inferior acid and base trapping capability. Thus, until a careful optimization study is carried out, it is recommended that the above procedures be carried out in their entirety. In addition, each batch of resin should be performance tested via separation of a standard sample and by running a blank determination as described in reference 11.

APPENDIX 2

COMPREHENSIVE LISTING OF RESULTS FROM INDIVIDUAL ABN AND SATURATE/NEUTRAL-AROMATIC SEPARATIONS

COMPREHENSIVE LISTING OF RESULTS FROM INDIVIDUAL ABN AND SATURATE/NEUTRAL-AROMATIC SEPARATIONS

Yields of acid and base fractions (tables 1 and 2) steadily increased during the development of the ABN method, largely through improvements in the resin preparation procedures (see Appendix 1) which resulted in materials with increasing capability to retain very weak acids and bases. Results in table 3 were obtained with the most current version of the ABN method.

Saturate/neutral-aromatic data (table 4) indicate both the precision and extensive application of the dual column procedure described in the body of the text.

TABLE A2-1. - Conditions for ABN separations

Boiling Range, °C	Run Number	Date	Sample, Wt (g)	Charge, Vol (mL)	Eluent	Volume of Eluent (mL)	
						Both Columns	Cation Column only
200-425	1	9/80	114.7	NA ¹	cyclohexane	1500	NA
	2	2/81	264.0	NA	cyclohexane	1500	NA
	3	8/82	250.5	650	cyclopentane	1675	335
	4	8/82	263.4	650	cyclopentane	1675	335
425-550	1	10/80	102.0	NA	cyclohexane	1500	NA
	2	3/81 ²	10.6	50	cyclohexane	125	25
	3	9/82	168.5	650	cyclohexane	1675	335
	4	9/82	171.0	650	cyclohexane	1675	335
	5	9/82	164.2	650	cyclohexane	1675	335
550-700	1	10/80	87.7	NA	cyclohexane	1500	NA
	2	3/81 ²	8.3	50	cyclohexane	125	25
	3	10/82	110.2	650	cyclohexane	1675	335
	4	11/82	113.0	700	cyclohexane	1675	335
	5	12/82	109.4	650	cyclohexane	1675	335
>700	1-Total	10/80	32.32	NA	cyclohexane	1500	NA
	2-Total	3/81 ²	4.1	50	cyclohexane	125	25
	3-Strong	10/82	126.2	800	benzene	1675	335
	4-Strong	10/82	124.9	800	benzene	1675	335
	5-Strong	11/82	125.3	800	benzene	1675	335
	6-Strong	11/82	128.3	800	benzene	1675	335
	3+4-Weak-I	11/82	--	700	25% benzene-	1675	335
	5+6-Weak-I	11/82	--	700	75% cyclohexane	1675	335
	3+4-Weak-II	12/82	--	700	25% benzene-	1675	335
	5+6-Weak-II	12/82	--	700	75% cyclohexane	1675	335

¹NA = data not available²These were small scale separations done with 0.9 x 74 cm columns

TABLE A2-2. - Results of ABN separations

Boiling Range, ° C	Run Number	Yield, Wt % of Distillate				
		Acids	Bases	Neutrals	Total	Total Acids and Bases
200-425	1	1.08	0.88	96.2	98.2	1.96
	2	3.18	1.30	94.4	99.0	4.48
	3	3.09	1.12	94.8	99.0	4.21
	4	3.25	1.02	94.2	98.5	4.27
	average ¹	3.17±.06	1.15±.10	94.5±.2	98.8±.2	4.32±.11
425-550	1	5.60	2.67	94.6	102.9	8.27
	2	5.98	3.50	89.70	99.2	9.48
	3	6.86	4.20	89.14	100.2	11.06
	4	6.85	3.99	89.00	99.8	10.84
	5	6.90	4.22	89.34	100.5	11.12
	average ²	6.87±.02	4.14±.10	89.2±.1	100.2±.2	11.01±.11
550-700	1	0.60	6.37	04.9	103.3	15.1
	2	11.12	6.55	82.85	100.5	17.7
	3	13.5	9.3	77.1	100.0	22.8
	4	11.0	11.4	78.7	101.1	22.4
	5	12.5	10.1	78.4	101.1	22.6
	average ²	12.3±0.9	10.3±.8	78.1±.6	100.7±.5	22.6±.2
>700	1-Total	32.5	27.1	48.6	108.2	59.6
	2-Total	43.5	32.3	36.7	112.4	75.8
	3-Strong	22.03	24.86	--	--	--
	4-Strong	21.26	23.35	--	--	--
	5-Strong	20.49	NA ⁴	--	--	--
	6-Strong	20.27	23.18	--	--	--
	average	21.0±.6	23.8±.7	--	--	--
	3+4-Weak-I	7.15	6.05	--	--	--
	5+6-Weak-I	7.69	6.45	--	--	--
	average	7.4±.3	6.3±.2			
	3+4-Weak-II	3.84	3.72	31.5	--	--
	5+6-Weak-II	4.64	3.95	31.4	--	--
	average	4.2±.4	3.8±.1	31.5±.1	--	--
	3+4-Total	32.6	33.9	31.5	98.0	66.5
	5+6-Total	32.7	33.6	31.4	97.7	66.3
	average ³	32.7±.1	33.7±.2	31.5±.1	97.9±.2	66.4±.1
Whole Crude ⁵	--	18.2	17.6	62.0	97.8	35.8

¹Average of Runs 2-4, uncertainties are average deviations²Average of Runs 3-5, uncertainties are average deviations³Average of Runs 3-6, uncertainties are average deviations⁴Not available⁵Calculated from results for >200°C distillates and residue plus the assumption that <200°C distillate was 100% neutrals. Distillate yields (whole crude basis) were: 2.59 (<200°C), 22.42 (200-425°C) 15.80 (425-550°C) 12.61 (550-700°C) and 45.36 wt % (>700°C).

TABLE A2-3. - ABN results on Cerro Negro fractions determined with the current (8/88) versions of the method

Boiling Range, °C	Fraction Yield (wt. %)			Total
	Acids	Bases	Neutrals	
425-550	11.37	3.82	84.64	99.83
>700	21.1(strong)	26.7(strong)	29.3	100 ¹
	14.3(weak)	8.6(weak)		
	35.4(total)	35.3(total)		

¹Data for weak acids and weak bases were normalized.

TABLE A2-4. - Results of saturate-aromatic separations (wt %)

Boiling Range, °C	200-425			425-550		
A. Whole Neutral Fraction Basis	<u>Saturates</u>	<u>Aromatics</u>	<u>Recovery</u>	<u>Saturates</u>	<u>Aromatics</u>	<u>Recovery</u>
	41.5	59.2	100.7	23.4	75.8	99.2
	41.7	60.2	101.9	22.1	77.2	99.3
	41.3	59.1	100.4	23.0	76.0	99.0
	41.1	58.6	99.7	22.0	74.9	96.9
	41.1	58.5	99.6	23.3	75.7	99.0
	41.1	57.8	98.6	23.5	75.7	99.0
	41.1	58.5	98.9	23.7	75.6	99.3
	41.1	59.8	99.6	23.3	75.7	99.0
	40.9	59.1	100.9	23.2	76.0	99.2
	41.1	58.9	100.0	23.1	76.1	99.2
	40.5	59.5	100.0	23.8	75.5	99.3
	41.2	58.8	100.0	23.9	75.3	99.2
	41.4	58.8	100.2	23.5	76.0	99.5
	41.0	59.6	100.6	23.7	75.3	99.0
	41.4	58.4	99.8	23.6	75.6	99.2
				23.3	76.4	99.7
				23.5	77.2	100.7
				22.7	76.7	99.4
				21.6	78.6	100.2
				22.5	77.6	100.1
Average	41.2	59.0	100.2	23.1	76.2	99.3
Standard Deviation	0.3	±0.6	0.7	0.6	0.9	0.7
B. Whole Distillate Basis	38.9	55.8	94.7	20.6	68.0	88.6

TABLE A2-4. - Results of saturate-aromatic separations (wt %), cont.

Boiling Range, °C	550-700			>700		
A. Whole Neutral Fraction Basis	<u>Saturates</u>	<u>Aromatics</u>	<u>Recovery</u>	<u>Saturates</u>	<u>Aromatics</u>	<u>Recovery</u>
	12.5	86.9	99.1	3.68	96.2	99.9
	12.7	86.6	99.3	3.71	95.8	99.5
	12.7	86.7	99.3	3.69	95.4	99.1
	12.7	86.7	99.4	3.66	95.8	99.5
	12.8	86.8	99.6	3.71	95.8	99.5
	12.8	87.7	99.6	3.78	95.2	99.0
	12.8	86.4	99.2	3.72	95.5	99.3
	12.4	87.1	99.5	3.75	95.0	98.8
	12.6	86.8	99.4	3.76	95.5	99.3
	12.9	87.0	99.9	3.74	93.6	97.3
	12.7	86.7	99.4	3.83	95.4	99.3
	12.5	86.8	99.3			
	12.7	86.7	99.4			
	12.5	86.9	99.4			
	12.7	86.6	99.3			
Average	12.7	86.7	99.4	3.73	95.4	99.1
Standard Deviation	0.2	0.2	0.2	0.05	0.7	0.7
B. Whole Distillate Basis	9.9	67.7	77.6	1.18	30.1	31.3
C. Whole Crude ¹	14.7	46.9	61.6			

¹The <200°C distillate was assumed to have saturate-aromatic ratios equal to those for the 200-425°C distillate for this calculation.

(This page intentionally left blank.)

APPENDIX 3
RELATIVE RESISTANCE OF NEUTRAL NITROGEN
COMPOUNDS TO HYDRODENITROGENATION

RELATIVE RESISTANCE OF NEUTRAL NITROGEN COMPOUNDS TO HYDRODENITROGENATION

Hydrotreating conditions: trickle-bed flow reactor containing Armak-840 Ni-Mo-alumina catalyst. See: O. K. Bhan, J. B. Green, and D. W. Brinkman, Am. Chem. Soc. Div. Petrol. Chem. Prepr., v. 32, 1987, pp. 361-368, for details.

Tables 1 and 2 show relative nitrogen contents of polar (acid + base) versus neutral fractions as a function of hydrotreating severity for Wilmington (California crude) and Mayan (Mexican crude) gas oils. Although absolute elemental nitrogen contents of both the total products and the neutral fractions decrease with increasing hydrotreating severity, the percentage of the remaining nitrogen contained in neutral fractions generally increases with severity for both gas oils. This trend indicates either exceptional resistance of neutral nitrogen types or their formation from acidic or basic types. Cerro Negro 200-425° C and 425-550° C distillates contained much higher relative proportions of neutral nitrogen than either of the gas oils shown here.

TABLE A3-1 - Nitrogen distribution in Wilmington gas oil and hydrotreated products

Sample No.	Hydrotreating Conditions		Elemental Nitrogen, wt %		Relative Nitrogen Content	
	T, ° C	LHSV	Total	Neutrals	Acid + Base ¹	Neutral ²
1693	----feed----		0.561	0.0532	90.5	9.5
2-2R	375	1.5	0.327	0.0282	91.4	8.6
2-10	375	1.25	0.306	0.0329	89.2	10.8
2-1R	375	1.0	0.304	0.0215	92.9	7.1
2-11	375	0.75	0.216	0.0276	86.7	13.3
2-3R	375	0.5	0.117	0.0132	88.7	11.3
2-6	400	1.5	0.171	0.0232	86.4	13.6
2-5	400	1.0	0.119	0.0166	86.0	14.0
2-4	400	0.5	0.0394	0.0076	80.7	19.3
2-7	425	1.5	0.0488	0.0070	85.7	14.3
2-8	425	1.0	0.0129	0.0016	87.0	13.0
2-9	425	0.5	0.0034	0.0012	64.7	35.3

$$^1 \text{Acid+Base N} = \frac{\text{Wt \% N (Total)} - \text{Wt \% N (Neutral Fraction)}}{\text{Wt \% N (Total)}}$$

$$^2 \text{Neutral N} = \frac{\text{Wt \% N (Neutral Fraction)}}{\text{Wt \% N (Total)}}$$

TABLE A3-2 - Nitrogen distribution in Mayan gas oil and hydrotreated products

Sample No.	Hydrotreating Conditions		Elemental Nitrogen, wt %		Relative Nitrogen Content ¹	
	T, ° C	LHSV	Total	Neutrals	Acid + Base	Neutral
1740	----feed----		0.202	0.011	94.6	5.4
MA-1-2	375	1.5	0.0515	0.0043	81.0	19.0
MA-1-1	375	1.0	0.0214	0.0013	93.9	6.1
MA-1-3	375	0.5	0.0096	0.0008	91.7	8.3
MA-1-4	400	1.5	0.0186	0.0037	85.6	14.4
MA-1-6	400	1.0	0.0137	0.0014	89.8	10.2
MA-1-5	400	0.5	0.0092	0.0015	83.7	16.3
MA-1-7	425	1.5	0.0071	0.0022	69.0	31.0
MA-1-9	425	1.0	0.0030	0.0010	66.7	33.3
MA-1-8	425	0.5	0.0016	0.0006	62.5	37.5

¹Calculated as in table A3-1.

Analysis of Heavy Oils:
Method Development and Application to Cerro Negro Heavy Petroleum
Detailed Separation and Analysis of Acidic Compounds

By

J. B. Green, S. K-T. Yu, J. A. Green
D. A. Doughty, J. W. Vogh, R. D. Grigsby

October 1989

Work Performed Under Cooperative Agreement No. FC22-83FE60149

Prepared for
U. S. Department of Energy
Assistant Secretary for Fossil Energy

W. D. Peters, Project Manager
Bartlesville Project Office
P. O. Box 1398
Bartlesville, OK 74005

Prepared by
IIT Research Institute
National Institute for Petroleum and Energy Research
P.O. Box 2128
Bartlesville, OK 74005

**DO NOT MICROFILM
THIS PAGE**

(This page intentionally left blank.)

TABLE OF CONTENTS

	<u>Page</u>
Foreword.....	iii
Abstract.....	xi
Acknowledgment.....	xi
Introduction.....	1
Acidic Compound Classes in Petroleum.....	2
Significance of Acidic Compounds.....	7
LC Separation of Acidic Classes.....	9
Analysis Techniques.....	23
Overall Assessment.....	30
Experimental.....	31
HPLC Conditions for Distillate Acid Fractions.....	31
HPLC Conditions for Acid Fractions from Distillation Residues or Whole Crudes.....	42
Removal of TMAH From Subfractions.....	44
Analysis of Subfractions.....	45
Results and Discussion.....	48
Separation and Analysis of SRC-II >325°C Strong and Weak Acid Concentrates.....	48
Separation and Analysis of Wilmington 370-535°C Acids.....	103
Effects of NIE Methodology on Subfraction Distributions.....	128
Summary of Results for Cerro Negro Acid Fractions.....	130
Conclusions.....	148
References.....	151

APPENDICES

Appendix 1.	Infrared-Chemical Derivatization Method for Determination of Total Hydroxyls and Carboxyls in Petroleum and Syncrudes.....	1-1
Appendix 2.	NMR-Chemical Derivatization Method for Determination of Acidic Functional Groups.....	2-1
Appendix 3.	Nonaqueous Titration of Acids.....	3-1
Appendix 4.	Retention Indices, Relative Response Factors, and Mass Spectra of Trifluoroacetate Esters of Phenolic Compounds Determined by Capillary GC/MS.....	4-1
Appendix 5.	High Resolution Mass Spectrometric Analysis of an HPLC Fraction Containing Difunctional Acids from an SRC-II Coal Liquid.....	5-1

TABLES AND ILLUSTRATIONS

<u>Table</u>	<u>Page</u>
1 Summary of acidic compounds identified in petroleum.....	3
2 Effects of alkyl and aromatic substitution on phenolic acidity.....	12
3 Acidity of single vs multifunctional compounds.....	13
4 Correlation of acidity versus retention in selected LC system.....	15
5 Retention of individual pyrrolic benzologs and ArOH in selected HPLC systems.....	19
6 HPLC conditions for distillable acids, ca. 1982-1984.....	32
7 Compounds in the ca. 1982-1987 acid standard blend.....	34

TABLES AND ILLUSTRATIONS

<u>Table</u>	<u>Page</u>
8 Current HPLC conditions for distillable acids.....	38
9 Compounds in the current acid standard blend.....	41
10 HPLC conditions for subfractionation of nondistillable acids.....	43
11 Summary of GC and GC/MS analysis conditions.....	47
12 Mass balances from separation of SRC-II >325°C.....	50
13 Infrared analysis of SRC-II >325°C acid subfractions.....	57
14 Results from GC/MS analysis of SRC-II 325°C+ whole weak acids and subfractions.....	58
15 Results from GC/MS analysis of SRC-II 325°C+ strong acid subfractions.....	75
16 Partitioning of selected compounds and homologs over the NIE and HPLC separations.....	85
17 Mass and elemental balances obtained from HPLC subfractionation of Wilmington 370-535°C total acids.....	105
18 Nonaqueous titration (NAT) results for Wilmington 370-535°C total acids and subfractions.....	106
19 Infrared results for Wilmington 370-535°C total acids and subfractions.....	108
20 NMR results for Wilmington 370-535°C total acids and subfractions.....	109
21 Heteroatom distributions in Wilmington 370-535°C total acids and subfractions calculated from elemental composition and NMR.....	110
22 Summary of compound classes present in Wilmington 370-535°C total acids and subfractions.....	112
23 Nonaqueous titration (NAT) results for Wilmington 370-535°C weak and strong acid concentrates and subfractions thereof.....	125
24 HPLC subfractionation mass balances as a function of NIE procedure and total acid yield.....	129
25 Mass balances from HPLC subfractionation of Cerro Negro acid concentrates from distillates.....	131
26 Mass balances from HPLC subfractionation of acid concentrates from distillation residues.....	132
27 Elemental content of Cerro Negro >700° C acid subfractions.....	137

<u>Figure</u>	<u>Page</u>
1 Analytical scale (ca. 30 µg) HPLC separation of SRC-II 325-425°C (dotted line) and Wilmington 370-535° C (solid line) acid fractions on silica with a mobile phase containing ethylene diamine (system 4, table 5).....	20
2 Analytical scale (ca. 30 µg) HPLC separation of SRC-II 325-425°C (dotted line) and Wilmington 370-535°C (solid line) acid fractions on silica with a conventional mobile phase (system 5, table 5).....	21
3 Analytical scale (ca. 30 µg) HPLC separation of SRC-II 325-425°C (dotted line) and Wilmington 370-535°C (solid line) acid fractions on silica with a mobile phase containing TMAH (system 6, table 5).....	22

TABLES AND ILLUSTRATIONS

Figure	Page
4 Preparative scale HPLC chromatograms of the standard blend (A, see table 7) and a Cerro Negro 200-425°C acid concentrate (NIE Run 2).....	33
5 HPLC chromatograms of the standard blend (table 7) as a function of TMAH concentration (A vs. B) and gradient profile (B vs. C). Δ_1 and Δ_2 indicate the difference in retention between components 3/5 and 9/10, respectively.....	36
6 HPLC chromatogram of Cerro Negro 200-425°C acids (NIE Run 4) obtained using current conditions (table 8). Compare with figure 4B.....	39
7 HPLC chromatogram of SRC-II >325°C strong and weak acid concentrates compared to that of the standard blend (table 7).....	51
8 HPLC separation of SRC-II >325°C weak acids compared to that of the current standard (table 9) using current conditions (table 8).....	53
9 HPLC separations of SRC-II >325°C strong acids and the standard blend in table 7. Conditions as specified in table 8.....	54
10 Comparison of GC/MS total ion current (TIC) and GC/FID chromatograms of whole SRC-II >325°C weak acids (table 14F).....	56
11 Mass spectrum of sterically hindered -8(O) ($C_{15}H_{22}O$) ArOH derivative in subfraction 3 from the SRC-II >325°C weak acid concentrate.....	89
12 Mass spectrum of a sterically hindered -14(O) ($C_{17}H_{20}O$) ArOH derivative in subfraction 4A from the SRC-II >325°C weak acid concentrate.....	90
13 Mass spectrum of a sterically hindered -16(O) ($C_{16}H_{16}O$) ArOH derivative in subfraction 4A from the SRC-II >325°C weak acid concentrate.....	91
14 IR spectra of SRC-II >325°C strong acid subfractions.....	92
15 GC/MS chromatograms of total ion current (A) and selected ion current at m/z 392 (B), of (acylated) subfraction 4 obtained from recent subfractionation of SRC-II >325°C strong acids depicted in figure 9.....	96
16 GC/MS total ion current (TIC) and selected ion current (SIC) chromatograms of (acylated) subfraction 3 from SRC-II >325°C weak acids.....	98
17 GC/MS total ion current (TIC) chromatograms of subfraction 4A from SRC-II >325°C weak acids before (A) and after (B) acylation.....	100
18 GC analysis of (acylated) SRC-II >325°C strong acid subfraction 5 with three-way detection.....	101
19 HPLC chromatograms of the current standard blend (A) (see table 9) and Wilmington 370-535°C composite total acid concentrate (B) obtained using conditions specified in table 8.....	104
20 Portions of IR spectra showing carbonyl bands in subfractions 1 vs. 4 from the Wilmington 370-535°C total acid concentrate.....	113
21 Correlation of the average number of carboxyl (O_2) groups per molecule indicated by elemental content vs. NMR, IR or NAT techniques.....	115

TABLES AND ILLUSTRATIONS

<u>Figure</u>	<u>Page</u>
22 Correlation of the average number of single oxygen functional groups per molecule indicated by elemental content vs. levels of specific functional groups detected by NMR or IR.....	116
23 Correlation of the average number of nitrogen atoms vs. NH functional groups per molecule.....	117
24 Correlation of the average number of sulfur atoms vs. NMR-determined SH/benzylic H groups per molecule.....	118
25 HPLC chromatograms of the standard blend (table 7) and Wilmington 370-535°C total acids obtained using initial conditions specified in table 6 ("B"-cutpoints). Compare with figure 19.....	121
26 Subfraction yields from separation of Wilmington 370-535°C total acids obtained with current (figure 19) vs. initial (figure 25) experimental conditions compared to yields from subfractionation of individual strong and weak acid concentrates obtained using initial HPLC conditions (figure 27).....	122
27 HPLC chromatograms from subfractionation of weak vs. strong Wilmington 370-535°C NIE acid concentrates.....	123
28 HPLC chromatograms of the standard blend (table 7) and a Cerro Negro 200-425° C acid concentrate (NIE Run 3) obtained using the CHCl ₃ -based mobile phase.....	134
29 HPLC chromatograms from subfractionation Cerro Negro >700° C° weak-II and strong acids.....	136
30 GC analysis of Cerro Negro 200-425° C acid subfraction 1 with three-way detection.....	138
31 GC analysis of Cerro Negro 200-425° C acid subfraction 2 with three-way detection.....	139
32 GC analysis of Cerro Negro 200-425° C acid subfraction 3 with three-way detection.....	140
33 GC analysis of Cerro Negro 200-425° C acid subfraction 4 predominantly ArOH) with three-way detection.....	141
34 GC analysis of Cerro Negro 200-425° C acid subfraction 5 with three-way detection.....	142
35 GC analysis of esterified Cerro Negro 200-425° C acid subfraction 5 with three-way detection.....	143
36 GC analysis of Cerro Negro 200-425° C acid subfraction 6 with three-way detection.....	144
37 GC analysis of esterified Cerro Negro 200-425° C acid subfraction 6 with three-way detection.....	145
38 GC analysis of whole Cerro Negro 200-425° C acids. Compare with figures 30-37.....	146

ABSTRACT

An HPLC method for fractionation of whole acid concentrates into nominal compound class subfractions is described. The method utilizes silica columns and gradient elution with eluents containing a strong base, tetramethylammonium hydroxide. The performance of the method is evaluated through analysis of subfractions obtained from a coal liquid, Wilmington, CA, petroleum and Cerro Negro heavy oil. Methods developed specifically for analysis of whole acid concentrates and subfractions are described in detail. These include: 1) an infrared method for determination of total hydroxyl and carboxyl groups after their conversion to trifluoroacetate and 2,2,2-trifluoroesters, respectively, 2) an NMR method for functional group analysis based on methylation of acidic groups with ^{13}C -enriched methyl iodide, 3) a nonaqueous titration procedure employing the potassium salt of dimethyl sulfoxide as a titrant for acidic compounds, 4) GC/MS analysis of hydroxyaromatic compounds after their conversion to trifluoroacetate esters, and 5) probe microdistillation high resolution mass spectrometric analysis of acid fractions exhibiting low volatility.

ACKNOWLEDGMENT

The financial support of the U.S. Department of Energy is gratefully acknowledged. The authors thank J. Y. Shay, S. Hamilton-Gassett, and R. Degraffenreid for their excellent elemental analysis of acid fractions. The authors also thank R. P. Anderson, W. D. Good, P. R. Stapp, and W. D. Peters for reviewing the manuscript. Finally, special appreciation is extended to Ms. Joan Haimson and the NIPER drafting department for manuscript typing and preparation.

**DO NOT MICROFILM
THIS PAGE**

(This page intentionally left blank.)

CONFIDENTIAL

DETAILED SEPARATION AND ANALYSIS OF ACIDIC COMPOUNDS

by

J. B. Green, S. K.-T. Yu, J. A. Green, D. A. Doughty, J. W. Vogh,
R. D. Grigsby, R. P. Vrana, J. S. Thomson, and L. Carbognani

INTRODUCTION

Whole acid fractions obtained from the nonaqueous ion exchange (NIE) liquid chromatographic procedure described in Chapter 2 typically contain three prominent compound types: carboxylic acids, hydroxyl compounds, and compounds containing an N-H group. For Cerro Negro acids, the available data (Chapter 2) indicate predominantly aliphatic hydrocarbon skeletons in the case of carboxylic acids, while compounds containing O-H and N-H groups are based on aromatic structures. The presence of additional heteroatoms in nonacidic moieties, e.g., thiophenic sulfur and ethereal oxygen, is supported by comparisons of elemental composition versus functional group analyses. The probability of additional heteroatom incorporation increases with boiling point, as does average aromaticity, prominence of N-H types, and overall yield of acid fractions. As noted in Chapter 6, metal-containing compounds in acid fractions from Cerro Negro 550°-700° C and >700° C boiling ranges do not exhibit spectra consistent with porphyrinic-type complexes. Although compounds containing thiol groups were not detected in acid fractions, low ppm levels of mercaptans were indicated earlier by standard methods applied to whole distillates (Chapter 1).

In order to further define the composition of major types as well as to improve detection and qualitative identification of minor types, a unified scheme was developed for analysis of acid fractions. Elements of the scheme include a method for subfractionation into compound types, and spectroscopic methods appropriate for analysis of each subfraction. Because of the significant amount of work involved in the development of each method, self-contained accounts of several of them are included as appendices. Although the scheme primarily addresses determination of compound classes present in whole acid fractions, in many cases the capability advanced to determination of individual homologs or compounds. The objectives of the work were development and verification of the scheme.

As part of the verification process, each element of the analysis scheme was applied to a variety of petroleum and syncrude fractions, including those from Cerro Negro. Since the work focused on development of methods rather than acquisition of compositional data, per se, emphasis is placed on data which most clearly illustrate the strengths/weaknesses of a given method, rather than those obtained exclusively on Cerro Negro fractions.

As was the case for base fractions (Chapter 4), acid concentrates from a Wilmington, CA 370-535° C distillate were used extensively for method evaluation due to the significant amount of prior work on it (1-6) and related distillates (7-10). Also, since this distillate served as the primary test sample during development of the NIE separation procedure, acid concentrates separated from it under a variety of conditions were in good supply. In fact, analyses of acid fractions were initially performed to determine the effect of modifications in the NIE procedure. The described analysis scheme evolved from this early necessity for determination of compound types in acid fractions obtained with varying NIE methods.

Acidic Compound Classes in Petroleum

Past work in analysis of acidic compounds in petroleum has resulted in identification of a number of compound classes, homologous series and individual compounds. Table 1 lists known classes of acids and provides representative structures for compounds in each class. Tentative or equivocal identifications are not included in the table.

Analysis of carboxylic acids began over 100 years ago. Lochte and Littman (11) briefly summarize the very early work and give detailed accounts of progress over the period from approximately 1920 to 1950. Using classical fractionation and identification methods, *n*-alkanoic acids containing up to 20 carbons and branched-alkanoic acids with up to 7 carbons were identified (11,12). Naphthenic (cycloalkanoic) acids containing one ring and up to 3 carbons in alkyl substituents were also identified (11,12). Bicyclic naphthenic acids were suspected but unconfirmed at that time.

TABLE 1. - Summary of acidic compounds identified in petroleum.

Type	Class	Representative Structures			
Carboxylic acids	Alkanoic	n -RCOOH	COOH (isoprenoid) ¹	COOH (branched, nonisoprenoid)	
	Naphthenic ²	COOH	COOH	(tricyclic terpenoid) ³	(steroid) ⁴ (hopanoic) ⁵
	Aromatic ³	COOH	COOH	COOH	COOH COOH
	Heterocyclic ³	(M - Ni or VO)	COOH	COOH	COOH
Hydroxyl compounds	Alcohols	HO			
	Hydroxyaromatics	HO	HO	HO	HO
Compounds containing N-H	Pyrrolic benzologs	H	H	H	H
	Amides	H		(major) ⁶	
Thiols	Aliphatic	n -RSH	RSH (branched)		
	Naphthenic	SH	SH		
	Aromatic ³				
Multifunctionals ⁶	Dicarboxylic	R (COOH) ₂	(COOH) ₂		
	Carboxypyrroles	COOH			
	Carboxyphenols	HO			

¹ Biomarker species corresponding to a given structure are noted in parenthesis.² Dominant class in most petroleum.³ In general the carboxylic acid group is not substituted onto the aromatic ring, but rather on R-groups or cycloalkane rings.⁴ Abundance of benzocarbazole isomers: [a] > [c] >> [b].⁵ None identified.⁶ ≈ 2 acidic groups.

Developments in modern instrumental techniques, especially mass spectrometry (MS), in the 1960's led to major advances in knowledge of petroleum composition. For example, Seifert and coworkers identified naphthenic carboxylic acids containing up to 5 condensed saturated rings as well as aromatic and heterocyclic species shown in table 1 (12-20). Also, individual compounds identical or related to carboxylic acids occurring in living organisms have been found in petroleum and oil shales (12,20-28). As noted in the table, identified compounds of biological origin include isoprenoid, tricyclic terpane, steroid and pentacyclic terpane (e.g., hopanoic) acids. Tricyclic terpanoid acids were prominent components in carboxylic acid concentrates isolated from the Cerro Negro 425-550° C distillate obtained in this work (28). On the whole, naphthenic acids predominate over other classes in crudes containing significant levels of carboxylic acids (≥ 0.5 wt %); on the other hand, alkanoic acids--both straight chain and branched (e.g., isoprenoid) chain--are often the prevalent carboxylic species in oil shales. Due to their significant water-solubility, lower molecular weight carboxylic acids are often present in refinery and production waste water streams (29,30).

Alkylphenols and other hydroxyaromatic (ArOH) homologs are the dominant hydroxyl compound class in petroleum. However, a series of 9-n-alkylfluoren-9-ols (benzylic alcohols) was recently identified in Athabasca bitumen (22,31). Because of their relatively low concentration in most crudes, much less effort has been expended toward analysis of ArOH in petroleum compared to coal tars and other coal-derived materials, which contain ArOH at levels up to 50 wt % (32). A comparison of ArOH concentrates from a Wilmington, CA, 225-370° C petroleum distillate containing 0.13 wt % ArOH versus a 200-325° C distillate from SRC-II coal liquid (15.5 wt % ArOH) revealed surprisingly similar distributions of homologs, with the petroleum concentrate exhibiting a higher degree of isomeric complexity in spite of its much lower concentration in the respective distillate (33). Although some authors have assigned highly condensed polyaromatic structures to single oxygen (nominally ArOH) compounds observed during high resolution MS (HRMS) analysis of petroleum fractions, only alkylnaphthols have been specifically identified (11,33). As indicated in the table, the major confirmed ArOH species are alkyl and/or phenyl substituted phenols, indanols, and analogous structures (7-11,33).

Pyrrolic benzologs and amides are the major classes of compounds containing the N-H functionality in petroleum. As indicated in the table, alkyl homologs of indole, carbazole, benzocarbazoles, and dibenzocarbazoles have been identified in crude oils (2,7-10,22,34-43). In addition, unsubstituted carbazole, benzo[a]carbazole, benzo[b]carbazole, benzo[c]carbazole, dibenzo[a,i]carbazole, and dibenzo[a,g]carbazole were identified in several crudes (37-40). The presence of unsubstituted pyrrolic benzologs in petroleum contrasts with the corresponding absence of nonalkylated members of many basic nitrogen series; for example, quinoline and benzoquinolines were not detected, yet a number of their alkyl homologs have been identified in crude oils (44). However, a documented identification of pyrrole or indole was not revealed in the literature search for this report. Furthermore, direct evidence for the presence of alkylpyrroles in crude oils is lacking, although they have been reported in analyses of synthetic crudes (45,46). The relatively low chemical stability of pyrrole, alkylpyrroles, and indole may explain their apparent absence in petroleum.

Group-type HRMS analysis of fractions enriched in pyrrolic-type compounds indicates presence of numerous indole-, carbazole-, etc.-based series containing one or more cycloalkane rings (2,7-10,22,41-43). Also, HRMS results generally indicate significantly broader carbon number distributions for a given aromatic type than GC-based methods. Since the number of possible isomers increases dramatically as the number of carbons in alkyl/cycloalkyl substituents increases, detection of higher homologs by GC becomes progressively more difficult with increasing carbon number since the total response is diffused over an ever-increasing number of isomers. Thus, the apparent greater diversity of types revealed by HRMS versus GC/MS results from the above effect, which also explains the shape of the typical GC/MS chromatogram--a series of resolved peaks superimposed onto a broad hump of unresolved (largely ignored) components. Cycloalkane-substituted pyrrolic benzologs are not explicitly shown in table 1 because the orientation and number of saturated rings has not yet been defined. However, based on HRMS data, they are present at levels comparable to species containing only aromatic rings.

Based on a general survey of papers addressing polar compounds in fossil fuels, pyrrolic benzologs (especially carbazole and higher homologs) are a prevalent compound class in virtually any type of crude or fuel. They appear to survive (or are formed during) any man-made or natural process applied to any hydrocarbon source containing detectable levels of nitrogen. In addition, recent findings indicate a greater diversity of structures than previously recognized. For example, two benzindole isomers were identified in coal derived liquids in addition to the widely recognized isomer, carbazole (47,48).

Evidence for amides in petroleum is largely indirect, e.g., their presence is frequently hypothesized from carbonyl bands in infrared spectra, titration results, and/or observation of NO-types in HRMS spectra (2-10,49-54). In spite of frequent references to this compound class, only 2-quinolones (table 1) have been identified in crude oil (55). Moreover, a subsequent attempt to verify the presence of this type and identify others using GC techniques was not successful (37). The obscurity of this class results from the wide range of structures consistent with the available data, their poor GC characteristics, the dearth of reference compounds and spectral data, occurrence of tautomeric forms (e.g., 2-hydroxyquinoline versus 2-quinolone), possibility of pseudo forms (e.g., 4-quinolone), and the significantly different liquid chromatographic (LC) behavior of the various amide subtypes (e.g., primary versus secondary versus tertiary or linear versus cyclic) which causes them to overlap into several fractions containing predominantly other acidic classes. Perhaps as the result of these factors, a much lower effort has been devoted to their analysis than the other classes discussed above.

Thiols (mercaptans) have primarily been detected and identified in light to mid-range petroleum distillates. However, their apparent absence in higher boiling range materials may simply reflect deficiencies in analytical techniques and/or destruction during distillation at higher temperatures. As noted in the table, acyclic and cyclic saturated thiols have been unequivocally identified, while only tentative identification of thiophenol in a Wasson, TX, crude was obtained (56). All of the identified compounds contained fewer than ten carbons. The percentage of the total sulfur present in thiol groups is generally quite low (56,57).

Although multiple heteroatom-containing compounds are readily detected in acidic fractions by HRMS (e.g., see Chapter 2), details of their structure have been defined in relatively few cases. Structures of compounds with two acidic groups shown in the table are largely based on the work of Siefert and Teeter, whose primary interest was carboxylic acids (19). The existence of other difunctional types is probable, but unconfirmed. The only commonly cited diacidic types in fossil fuels are dihydroxyl compounds found in coal-derived liquids.

With the exception of sulfonic acids and other SO_xH types, virtually all common types of organic acids have been identified in petroleum. Total acid content and distributions of acidic types have been determined for relatively few crudes and boiling ranges (4,6). Few trends are evident from those data, except that oxygen- and nitrogen-based functional groups are present in much greater abundance than thiol or other sulfur-based acidic types. Also, it is generally recognized that crudes from Venezuela, Romania, and California typically contain carboxylic acids at levels an order of magnitude higher than typical domestic or mid-east crudes (11,12,28).

Significance of Acidic Compounds

As with most nonhydrocarbon types, the impact of acidic compounds on petroleum properties and utilization is predominantly negative. For example, naphthenic acids contribute to corrosion of distillation towers in refineries (58).

Several studies have shown pyrrolic benzologs, especially alkyl-carbazoles, to be more resistant to hydrodenitrogenation than basic nitrogen compounds (59-61). Carbazole, benzocarbazole, and their alkylhomologs are also dominant nitrogen-containing components in clarified slurry oils, thereby indicating low reactivity and/or formation during cat-cracking processes (62). Pyrrolic benzologs, especially alkylindoles, which survive the various refining processes and end up in finished products have been reported to be major contributors to gum formation (63-66). Furthermore, gum formation is catalyzed by compounds with comparable or greater acidity than that of carboxylic acids (64,67).

Overall, acidic compounds in $>500^{\circ}\text{C}$ petroleum resids exhibited the lowest degree of conversion during hydrotreating (68). Similarly, the prevalence of acidic compounds, especially ArOH, in coal liquefaction (32) and petroleum resid-coal coprocessing (69) products produced at high temperatures and pressures attests to their chemical stability. ArOH contributed to sediment formation during storage of SRC-II coal liquid via oxidative coupling reactions (70). Phenolic coupling also contributes to sediment formation in storage of petroleum middle distillates (71,72).

Current specifications (73) for total acidity, expressed in terms of neutralization equivalents (mg KOH/g fuel), are 0.1 and 0.015 for commercial and military jet fuels, respectively. Corresponding limits for thiols are extremely low: 0.003 and 0.001 wt % S as SH types. Thiols are specifically limited because of their corrosive properties and adverse effect on fuel system elastomers (74). Naphthenic acids attack zinc present in fuel storage and/or handling systems to form zinc naphthenates, which promote water suspension due to their surfactant properties (73). The presence of water increases corrosion and icing problems in aircraft fuel lines and filters.

Thermal stability of jet fuels is inversely related to total acidity (75). These authors state that total acid content, as determined by NIE, is the best predictor of thermal stability examined to date. Differential scanning calorimetric measurements of exothermic reactions in the presence of oxygen revealed a significantly higher ΔH for the acid fraction from a jet fuel compared to the base and neutral fractions or the fuel itself (76). Acid fractions from jet fuels typically contain a relatively high proportion of ArOH, which were shown to form deposits during thermal stability studies of coal-derived naphtha (77).

In summary, indigenous acidic compounds increase corrosion and resist removal during refining processes. They also decrease storage and thermal stability of distillate products and accelerate degradation of selected fuel handling/delivery components. Many potential adverse effects of acidic compounds, such as catalyst deactivation, emulsion stabilization, and tendency toward coking and fouling have not been investigated in detail. Also, their impact on product quality is incompletely understood.

Carboxylic acids are the most beneficial acidic type present in petroleum. Besides their adverse effects discussed above, they improve lubricity of jet fuels (78), behave as surfactants in secondary and tertiary crude oil recovery processes (14), and serve as biological markers for use in geochemical correlations (12). In addition, petroleum-derived naphthenic acids have commercial value for use in paints, wood preservatives and cutting fluids for metal working (11). Hindered phenols potentially contribute to antioxidant properties observed for polar compounds in selected fuels (79); however, their behavior as such remains to be proven. Properties of acidic compounds normally considered to be detrimental, e.g., high viscosity and boiling point, are beneficial with respect to asphalts, which are frequently air-blown to increase acid content via oxidation.

Current knowledge of the significance of acidic compounds in petroleum is limited by analytical methodology, especially the capability to detect and identify trace components in products, and past reliance on gross parameters such as elemental and asphaltene content.

LC Separation of Acidic Classes

This section discusses liquid chromatographic (LC) methodology for separation of acids into compound classes, as well as structural effects governing their elution behavior. Although solvent extraction techniques were employed in early attempts to isolate and purify acidic classes (11,35), normal phase LC later became the technique of choice due to its greater flexibility and efficiency (see Chapter 2).

Alumina is the most commonly used adsorbant for LC separation of acids into compound classes. McKay et al., used size exclusion liquid chromatography (SEC) initially to separate carboxylic acids followed by LC on basic alumina for separation of pyrrolic benzologs, ArOH, and amides, respectively, from whole acid concentrates obtained from several petroleum distillates (2). SEC separation of carboxylic acids is based on their tendency to dimerize in weak-medium polarity solvents, which effectively doubles their apparent molecular size relative to other acidic types (80,81). The need for their removal prior to alumina chromatography arises from their essentially irreversible adsorption onto alumina, which prevents their recovery (82).

The elution order of acidic classes on alumina determined by Snyder et al. (8-10,82-84) generally confirms that given above. Since their data indicated significant overlap of acidic classes on alumina alone, Snyder et al. employed subsequent LC separations on silica and charcoal to simplify the composition of the initial alumina fractions.

The general ease of elution for acidic classes on alumina--pyrrolic benzologs >ArOH >amides >>carboxylic acids--has been verified many times over in subsequent work. For example, many of the schemes reviewed in table 4 of Chapter 2 employed alumina for this purpose. Use of silica in place of alumina results in a similar elution order and selectivity (85,86). One advantage of silica is that carboxylic acids may be recovered with alcohol-containing mobile phases, whereas with alumina they are irreversibly adsorbed. Its main disadvantage is the required use of low polarity eluents for separation of pyrrolic benzologs and ArOH due to their weak interaction with silica.

Subsequent evaluations of silicas bonded with amino-, cyano-, nitro-, and sulfonic acid-containing moieties did not reveal any significant advantage of those materials over plain silica or alumina for separation of acidic compound classes (87-91). However, it should be noted that the bulk of those evaluations were carried out with pure compounds rather than actual petroleum fractions. The effectiveness of a given LC column packing material may be reliably predicted from pure compound data only if representative members of each class are included to show steric and electronic effects on elution behavior. These effects are briefly discussed below.

Steric hindrance of functional groups by alkyl groups or other moieties decreases retention in proportion to their interference with the functional group-adsorbent interaction. For example, studies of alkylphenol retention on plain and bonded phase silicas show their elution to depend on the number and size of o-substituents (91-95). The effect of steric hindrance can be quite dramatic; for example, 2,6-di-t-butylphenol elutes as an unretained compound in many systems where phenol itself is strongly retained. Steric effects for other acidic types have not been investigated in detail.

In cases where hydrogen-bonding is the dominant solute-adsorbent interaction, electronic effects increase or decrease retention according to their impact on the strength of the hydrogen bond. Since acids function

primarily as hydrogen donors, effects on acidity, indicated by pK_a , parallel chromatographic behavior whenever steric effects are absent or factored out separately. Using phenol as an example, table 2 illustrates the effects of alkyl substitution (decreases acidity at o- and p-positions, negligible at m-positions) versus increased aromaticity (opposite of alkylation) on acidity. Acid dissociation constants (pK_a) are taken from the literature (96). The data in the table explain the decreased retention of p-alkylphenols relative to phenol and the increased retention of naphthols and 3- or 4-phenylphenol in most normal phase LC systems (91-95). For 2-phenylphenol and many analogous cases, the observed retention reflects offsetting steric versus electronic effects. As noted in Chapter 4, the electronic effects of alkylation and aromaticity on base retention are exactly opposite those for acids, since in that case solutes act as hydrogen acceptors rather than donors.

Corresponding effects for other acidic classes tend to be less than or equal to those for phenol (96). For example, the differences in pK_a for o-, m-, and p-thiocresols versus thiophenol are less than those for the corresponding phenols. Phenyl substitution at the alpha carbon lowers pK_a 's of aliphatic carboxylic acids by about 0.5 unit, which is comparable to the difference in pK_a between phenol and phenylphenols. The effect of phenyl substitution at beta and more distant positions from the carboxylic group is proportionately less. The pK_a 's of cyclohexanecarboxylic, cyclopentanecarboxylic and n-hexanoic acids range between 4.85-4.91. 1-Methylcyclohexanecarboxylic acid exhibits a slightly higher pK_a of 5.13. Benzoic acid, which as noted earlier is atypical of most carboxylic acids in petroleum, exhibits a pK_a (4.20) about 0.8 unit lower than most aliphatic carboxylic acids.

The presence of additional heteroatoms generally increases the acidity of a given functional group via inductive or other electronic effects. However, the magnitude of these effects strongly depends on the orientation and types of functionalities involved. Also, many pK_a shifts for multifunctional compounds result from formation of zwitterions and other effects occurring only in aqueous media. Obviously, those phenomena are not relevant to the present topic. Table 3 lists representative examples of the effect of additional heteroatoms/functional groups on the acidity of carboxyl, hydroxyl, and N-H types. In terms of chromatographic behavior, the possibility of multiple interactions with the adsorbent must be considered in addition to effects on acidity for multifunctional compounds.

TABLE 2. - Effects of alkyl and aromatic substitution on phenolic acidity.

9.99 ¹ ↓	<u>o</u> - 10.26 <u>m</u> - 10.00 <u>p</u> - 10.26 ↓	<u>o</u> - 10.2 <u>m</u> - 10.07 <u>p</u> - 10.0 ↓	<u>o</u> - 10.62 <u>m</u> - 10.12 <u>p</u> - 10.23 ↓
<u>o</u> - 9.55 <u>m</u> - 9.63 <u>p</u> - 9.55 ↓	2,6 - 10.59 2,4 - 10.58 2,3 - 10.50 3,4 - 10.32 2,5 - 10.22 3,5 - 10.15 ↓
α - 9.30 β - 9.57	2,4,6 - 10.88 2,3,4 - 10.59 2,4,5 - 10.57 3,4,5 - 10.25		

¹pK_a at 20° or 25° C

TABLE 3. - Acidity of single vs multifunctional compounds.

4.20 ¹	4.75	4.45	4.10	1) 4.08 2) 9.85 ²	1) 3.62 2) 4.60

4.84	4.67			1) 3.77 2) 6.08

9.99	9.65	1) 9.44 2) 12.32	9.00	8.72	8.54

-16.5	14.2				

¹pK_a at 20° or 25° C

²pK_a for dissociation of second acidic group

Table 4 compares the acidity (pK_a) of compound classes with order of elution in the relatively few LC systems where their behavior is sufficiently well defined. The bulk of the retention data for acidic compounds in the literature could not be incorporated into the table because, for a given set of conditions, only a single class or an inadequate number of compounds or classes were considered. Also, by necessity the pK_a range given for weakly acidic classes is based on limited data (83,96-99). Acidities in dimethyl sulfoxide (DMSO) (100) were consulted in some cases to confirm trends suggested by aqueous pK_a 's. Relative retention on alumina is based on a calculated parameter, ϵ_1 , derived by Snyder and Buell for petroleum-derived acids as a function of boiling range (82,83). Although ϵ_1 is a useful guide for predicting relative elution order, it cannot generally be used to predict the degree of overlap between classes with similar values of ϵ_1 or other specific aspects of chromatographic behavior obtainable with a given batch of alumina or a particular solvent sequence. Retention times on silica in conjunction with the various eluents were obtained in this laboratory (85,101-104), with exception of those for DMSO-containing mobile phases (90,105,106). Data for severely hindered or otherwise atypically eluting species were not used in setting limits of elution for compound classes. Where possible, results from actual petroleum fractions were used to define limits for elution of a given class. Incompletely defined limits are denoted by appropriate symbols: $<$, $>$, $\sim$.

Overlap in pK_a between classes is minimal, except for pyrrolic benzologs and selected alcohols/ketones. Thus, for the idealized case where separation occurred solely according to the acidity of the compounds present, fractionation of the major acidic classes in petroleum would be straightforward and the majority of the resulting fractions would contain a single class. In actual practice, elution of the major classes--pyrrolic benzologs, $ArOH$, and carboxylic acids--does follow their relative acidity in most of the LC systems in the table. However, their elution regions frequently overlap each other as well as those of minor classes. Also, some classes are retained out of proportion to their acidity. For example, the comparably strong retention of amides (pyridones and quinolones) observed in most cases may be rationalized from the presence of two heteroatoms capable of interaction with the adsorbent. However, the anomalously weak retention of thiols, relative to other types of comparable acidity, shows that additional factors must be taken into account to adequately explain relative adsorptivities of functional groups. Snyder addresses this subject in detail in his book (107).

TABLE 4. - Correlation of acidity versus retention in selected LC systems

Compound Class or Subclass	Approximate pK_a Range ¹	Retention Time or Index					
		Al_2O_3 (3.8% H_2O) ²	SiO_2 (plain) ³	SiO_2 ($CH_3(CH_2)_8COOH$ modified) ⁴	SiO_2 (DMSO modified) ⁵	SiO_2 (ethylene diamine modified) ⁶	SiO_2 (TMAH modified) ⁷
Neutrals	-	(-0.1)-0.3	2-7	2-7	0.2-0.5	1-3	<2
Pyrrolic benzologs	12-14	0.3-0.4	7-14	7-14	<3-4	4-10	<2-10
Cyclic benzylic alcohols and ketones ⁸	12-14	0.3-0.4	<14-(~20)	-	~3	-	4-7
Pyridones, quinolones ⁹	11-12	0.6-0.8	>30	>30	-	~20	15-30
Aliphatic thiols	10.5-11.5	0.01-0.03	-	-	-	-	-
ArOH	9-11	0.4-0.7	<14-27	<13-24	<4-8	7-18	9-30
ArSH	6-7	0.5-0.7	-	-	<0.5	-	-
RCOOH	4.5-5.5	>1.0	>pyridones, quinolones	<24	<4-5	>20	30-35
ArCCOOH	3.5-4.5	>1.0	>pyridones, quinolones	24-29	>8	>20	35-40
$R(COOH)_2$	3.5-5.0	>1.0	>pyridones, quinolones	-	-	>20	>45

¹Refs. 83, 96-100. See Text.²Refs. 82, 83.³Refs. 22, 85, 101⁴Refs. 85, 101.⁵Refs. 90, 105, 106.⁶Ref. 91 and unpublished data.⁷Refs. 42, 102-104.⁸e.g.: 2-indanone, 2-tetralone, 9-fluorenone.⁹ pK_a 's of most other amides are >12.

The main parameter for adjusting separation selectivity is mobile phase composition. The results for the various silica-based systems in the table reveal the significant impact of relatively minor differences in eluent composition on retention of selected acidic classes. For example, although carboxylic acids were strongly retained on silica with a conventional solvent gradient (system designated as "plain SiO_2 " in the table), addition of 0.0268 M n-decanoic acid to the mobile phase ($\text{CH}_3(\text{CH}_2)_8\text{COOH}$ -modified system) greatly accelerated their elution relative to other acidic types (85). The effect of DMSO (DMSO-modified SiO_2) was similar to that of decanoic acid (105). On the other hand, addition of aliphatic amines to eluents increased retention of pyrrolic benzologs relative to ArOH , which resulted in greater overlap of those classes (91). The selectivity observed for silica using a mobile phase spiked with 0.1% ethylene diamine (see table) is very similar to that obtained with covalently bonded amine columns (91). In either case, retention of pyrrolic benzologs, aromatic amines and other N-H types is enhanced relative to that on plain silica. Tetramethylammonium hydroxide (TMAH) and related compounds effect the greatest change in the chromatographic properties of silica observed to date. For example, the bulk solvent strength required for elution of acidic N-H and OH types on silica increased dramatically whenever the mobile phase contained 0.0015 M TMAH (102). TMAH and alkali metal hydroxides react with silanol groups to form silicate salts (108). This imparts a basic character to the surface which causes acidic compounds to be more strongly adsorbed. TMAH also interacts with solutes in the mobile phase. For example, TMAH accelerates elution of carboxylic and other relatively strong acids via association in solution (102). Corresponding effects of eluent composition for selectivity on alumina have not been investigated.

The current state of the art is such that, while some LC systems and/or types of columns may definitely be excluded from serious consideration, insufficient data exist to support a clear choice among others. The ability of a given column packing to separate acidic compound classes depends on its inherent affinities for each functional group versus its sensitivity to structural effects. Thus, a material exhibiting a lower degree of selectivity for parent members of two classes, e.g., pyrrole versus phenol, could outperform another with a higher selectivity if its sensitivity to steric and electronic factors was significantly less. The main deficiency in much of the prior work is failure to adequately address structural effects on separation

behavior and their corresponding impact on the quality of fractions obtained. Therefore, selection of a LC system for use in work for this chapter was largely based on pragmatic rather than theoretical considerations. These are outlined below.

Alumina was rejected as a potential adsorbent for the following reasons.

- Limited availability. High grade microparticulate alumina is not widely available due to the nearly exclusive use of silica and polymer-based packings in HPLC (high performance LC). Also, preparative grade silica (10-20 μm , irregular particles) may be purchased for around \$250 per Kg, whereas 10 μm alumina typically sells for \$75 per 10 g. The available low cost bulk grade alumina is suitable only for low efficiency open column LC.
- Limited column life. Previously cited separations on alumina employed classical techniques with fresh alumina for each separation. Given its sensitivity to eluent water content (107) and tendency toward irreversible adsorption of carboxylic and other strong acids, it appeared doubtful that a single column could exhibit stable elution behavior throughout extensive calibration and subsequent application to petroleum fractions, especially given the wide polarity range of solvents required.
- Limited sample capacity. For a given pore size, the surface area of silica exceeds that of alumina by about a factor of three. Sample capacity is directly related to the available surface area (109).
- Prior experience. Problems and disadvantages cited above led to the abandonment of an alumina-based method for separation of aromatic hydrocarbons by ring-number (110) in favor of the DNAP-silica procedure described in Chapter 5A, in spite of the excellent selectivity obtained on alumina. In addition, preparation of efficient alumina columns with reproducible separation characteristics proved to be difficult and costly.

In keeping with the philosophy discussed in other chapters of using only the best available separation technology for work on Cerro Negro, the decision was made to develop an HPLC method for subfractionation of acids instead of using open column LC. The existing classical alumina-based techniques could not be readily adapted to HPLC, for reasons listed above. Of the silica-based approaches, the combination of plain silica and mobile phases containing TMAH showed the greatest promise. For example, the increased retention of acids on TMAH-treated versus plain silica enabled use of more polar solvents for

elution. This was a significant advantage because of the limited solubility of acids in weak eluents such as hexane. Also, preliminary evaluations indicated that TMAH-treated silica provided superior resolution of acidic classes.

Table 5 compares resolution of individual pyrrolic versus ArOH compounds in several HPLC systems. Based on the literature survey, separation of sterically hindered ArOH from pyrrolic benzologs was anticipated to be a severe test of the relative capability of a given method. Inspection of the table reveals that while only marginal resolution of these classes is obtained in any of the systems, the best separations are clearly achieved with plain silica using conventional or TMAH-spiked eluents (systems 5 and 6). Also, the order of elution within each class reflects steric and electronic effects discussed earlier.

Further evaluation of LC systems in table 5 was carried out with actual acid fractions. Figures 1-3 compare separation of a Wilmington, CA, 370-535° C acid fraction with another from a 325-425° C SRC-II coal liquid distillate in LC systems 4-6, respectively. The Wilmington fraction was isolated with a prototype NIE procedure; the SRC-II acids were obtained from extraction with aqueous-alcoholic 2 M NaOH. The SRC-II fraction contains predominantly ArOH and dihydroxyaromatics ($\text{Ar}(\text{OH})_2$), since weaker acids generally do not extract (101). The Wilmington fraction contains most or all types listed earlier in table 1; however, the pyrrolic types predominate in the chromatograms owing to their high UV response.

Comparison of the figures reveals the superior performance of the silica-TMAH system (No. 6, table 5) in resolving pyrrolic versus ArOH classes as well as the more strongly retained carboxylic and $\text{Ar}(\text{OH})_2$ types. For example, Wilmington ArOH are clearly discernible in the chromatogram obtained with the TMAH system (figure 3), whereas they apparently elute as a tail on the pyrrolic benzolog peak in the other two systems. The degree of overlap between SRC-II ArOH and Wilmington pyrrolic benzologs is also significantly lower in figure 3. Furthermore, the small quantity of pyrrolic compounds in the SRC-II fraction is widely separated from ArOH in the TMAH-spiked system, while only marginally so in the others. As indicated by data in table 5, corresponding separations of pyrrolic versus ArOH classes using systems 1-3 were inferior to any of those in figures 1-3. In addition, the generally superior performance of the TMAH-silica system was evident in similar comparisons of acid fractions obtained from a wide variety of petroleums and synfuels.

TABLE 5. - Retention of individual pyrrolic benzologs and ArOH in selected HPLC systems

Nc.	1	2	3	4	5	6
Column Type	Cyano bonded phase	Amino bonded phase	Silica (n-butylamine (BA) modified)	Silica (ethylene diamine (EDA) modified)	Silica ("plain")	Silica (TMAH modified)
Mobile Phase						
A:	n-hexane	n-hexane	n-hexane	n-hexane	n-heptane	MTBE ¹
B:	ethyl acetate	ethyl acetate	MTBE contg. 2% MeOH, 0.15% BA	MTBE contg. 2% MeOH, 0.10% EDA	CH ₂ Cl ₂ contg. 0.3% EtOH	60% MTBE, 40% MeOH contg. 0.0015 M TMAH
Gradient	1→25% B in 30 min.	2→75% B in 33 min.	4→100% B in 40 min.	4→100% B in 40 min.	1→100% B in 30 min.	2→100% B in 50 min.
Reference for detailed experimental conditions	91 (table 12)	91 (table 12)	91 (table 9)	91 (table 9)	85 (table 1)	102 (table 2)
Compound	Retention time (min.)					
1,2,3,4-Tetrahydrocarbazole	6.98	11.5	6.30	14.0	11.3	4.13
2,3-Dimethylindole	7.38	11.8	6.56	14.4	11.8	4.80
3-Methylindole	7.62	12.8	7.04	15.5	12.0	6.06
Indole	8.64	13.7	8.04	16.1	13.2	8.10
2-Methylcarbazole	8.30	13.0	7.20	15.6	12.8	6.36
Carbazole	9.16	14.0	7.84	16.2	12.3	7.70
13H-Dibenzo[a,i]carbazole	13.0	16.3	9.14	19.5	13.5	9.43
2,6-Dimethylphenol	5.88	11.2	5.86	15.5	14.2	9.63
2,4-Di- <u>sec</u> -butylphenol	6.82	13.3	6.98	16.8	16.1	9.20
2,4,5-Trimethylphenol	7.96	16.2	8.42	19.0	20.2	14.3
2,3-Dimethylphenol	8.22	16.5	8.40	19.4	20.0	16.8
<u>o</u> -Cresol	8.28	17.7	8.62	20.9	20.0	18.8
Phenol	9.57	22.2	10.4	25.6	25.0	23.2
2-Naphthol	11.4	28.2	11.9	33.9	24.9	28.3

¹ Methyl t-butyl ether.

FIGURE 1. - Analytical scale (ca. 30 μ g) HPLC separation of SRC-II 325-425°C (dotted line) and Wilmington 370-535° C (solid line) acid fractions on silica with a mobile phase containing ethylene diamine (system 4, table 5). The region corresponding to Wilmington ArOH is crosshatched; Ar(OH)₂ and carboxylic acid classes do not elute. See text.

FIGURE 2. - Analytical scale (ca. 30 μ g) HPLC separation of SRC-II 325-425°C (dotted line) and Wilmington 370-535°C (solid line) acid fractions on silica with a conventional mobile phase (system 5, table 5). The region corresponding to Wilmington ArOH is crosshatched; (ArOH)₂ and carboxylic acid classes do not elute. See text.

FIGURE 3. - Analytical scale (ca. 30 μ g) HPLC separation of SRC-II 325-425°C (dotted line) and Wilmington 370-535°C (solid line) acid fractions on silica with a mobile phase containing TMAH (system 6, table 5). The region corresponding to Wilmington ArOH is crosshatched; Ar(OH)₂ and carboxylic acid classes elute as shown, except that SRC-II components eluting in the region designated "RCOOH" are actually hindered Ar(OH)₂ types. See text.

Thus, selection of TMAH-modified silica for subfractionation of Cerro Negro acids was based on its qualitatively superior performance in analytical scale evaluations and the following practical advantages.

- HPLC compatibility. The use of silica in combination with in-situ TMAH modification simplified scale-up to preparative separations, since silica columns are commercially available in a variety of sizes and/or easily prepared in-house. Also, column-to-column variation and changes in column performance with use can largely be compensated for by appropriate adjustments in TMAH concentration.

- Stability. Since TMAH is continually present in the mobile phase, this system exhibits very consistent retention characteristics compared to most normal phase HPLC systems. This feature enables careful calibration of a given column prior to use and provides for uniform separation selectivity over time.

- Sample solubility. The relatively strong solvents (ether, chloroform, methanol) required for elution of acids from TMAH-modified silica, and potentially TMAH itself, promote solubilization of acid fractions. Acid fractions typically contain the most polar and therefore least soluble compounds present in petroleum or synfuels.

Its major disadvantages are 1) the necessity of removing TMAH from the resulting fractions and 2) a relatively high sensitivity to steric effects. These are discussed in detail in later sections.

Analysis Techniques

Analysis for acidic compounds may be performed on whole distillates or crudes, concentrates from various methods for isolating total acids, or more refined fractions containing predominantly one class. By far, the most commonly performed analysis is determination of total acidity via titration with base after ASTM D 664 or an analogous method.

Normally, the degree of detail obtained in an analysis is related to the effort expended on preseparation. However, recent efforts toward selective detection of acidic compounds have reduced or eliminated the need for prior separation in selected cases. For example, ammonia chemical ionization GC/MS was used to determine carbazole and benzocarbazole homologs directly in

clarified slurry oils (62). Similarly, GC coupled with microwave-induced plasma detection of elemental oxygen was used for direct determination of phenols in coal liquids (111). However, the prominence of those types in their respective samples and, in particular, the absence of interfering basic/neutral nitrogen or oxygen compounds were essential to the success of either approach. Carboxylic acids were selectively detected by GC/MS with fast atom bombardment ionization (29). Also, several chemical derivatization approaches have been employed to increase specificity and/or sensitivity for acidic compounds in infrared (IR), NMR, and MS analyses in the presence of hydrocarbons and other interferences. These are discussed in detail in the appendices describing the various analytical techniques. Nevertheless, in the more general case where both nonacidic and acidic components are of interest, or where identification of unknown or nontargeted species is desired, compound class separation remains a crucial step in the overall analysis.

IR spectroscopy is the standard technique for determining acidic compound types in a given fraction. However, it suffers from three significant limitations. 1) The molar absorptivity (ϵ) of a given functional group depends on its chemical environment; e.g., ϵ varies with solute structure and solvent type. 2) Intermolecular interactions can significantly change the intensities (ϵ) and frequencies of IR bands corresponding to participating functional groups. 3) Spectral overlap between bands from various carbonyl-containing functional groups greatly complicates qualitative and quantitative interpretation of that IR region (1800-1630 cm^{-1}). Of these, the first is the most severe because variation of ϵ with structure practically limits the accuracy attainable from IR. The adverse effects of the other two can be minimized via appropriate selection of experimental conditions, such as the solvent employed, as well as with sample modifications; e.g., through chemical derivatization, neutralization or chromatographic separations.

Shortcomings in IR have spurred development of alternate approaches for determination of acidic functional groups. For example, numerous approaches utilizing NMR in conjunction with chemical derivatization have been developed. Unlike IR, NMR response is based solely on nuclear abundance; for the most part, chemical environment affects only chemical shift and not signal intensity. This approach is limited only by deficiencies in the chemical derivatization, e.g., incomplete reaction or interference from excess

reagents, and spectral overlap in reacted functional groups. The most appropriate reactions for this approach are those which incorporate NMR-compatible nuclei which are not present in petroleum, e.g., ^{31}P , ^{19}F , ^{29}Si , and ^{119}Sn . However, reactions resulting only in the addition of ^{13}C or ^2H may be employed if the reagents are significantly enriched in those isotopes and corrections are made for their natural abundance in petroleum. A practical disadvantage of NMR is the fairly large, typically $>0.1\text{g}$, sample size required.

Although generally less specific than IR or NMR techniques, nonaqueous titration (NAT) methods may be used for determination of acidic types under favorable conditions. Examples include: 1) determination of thiols with silver nitrate (UOP Method 163-80), owing to the high selectivity obtained for thiols with that method (57), 2) determination of ArOH in coal liquids, due to their predominance over other acidic types in coal-derived materials (112-114), and 3) determination of carboxylic acids in petroleum and bitumen, made possible by virtue of their significantly greater acidity than other types commonly present. Alternately, acidic types may simply be defined in terms of their titration behavior--e.g., strong, weak, very weak, etc.--without regard to functional groups as defined in the conventional manner (114-116).

IR, NMR, and NAT techniques and applications are reviewed in detail in Appendices 1-3.

UV spectrophotometry has also been employed for determination of acidic types, classes and subclasses. However, its use has declined significantly in recent years owing to the greater popularity of other instrumental methods discussed above. For example, UV was commonly used for qualitative identification of pyrrolic compounds in early work (34,35,117). Snyder et al. made extensive use of UV for determination of indole, carbazole, and benzocarbazole homologs in their LC fractions (8-10,36). Because of their strong UV absorption and relatively characteristic spectra, pyrrolic benzologs are more amenable to UV analysis than other acidic types. In addition, fluorescence techniques have been used to distinguish isomeric benzocarbazole and dibenzocarbazole ring structures (2,38).

Sporadic mention of qualitative and semiquantitative analyses (spot tests) for acidic functional groups occurs even in recent papers (e.g., (66)). The tests have not seen extensive use in petroleum chemistry because

of the difficulty in obtaining fractions sufficiently pure for testing, and because the wide range of isomers of a given type present increases the difficulty in distinguishing positive versus negative results. Similarly, quantitative colorimetric methods, which are typically based on chemistries employed in qualitative tests, are very seldom employed.

MS almost invariably plays a key role in analyses carried beyond the stage of compound class assessment into determination of specific homologs or individual components. Three common approaches in MS analysis are: 1) comprehensive analysis of a relatively "pure" fraction using GC or batch sample introduction and a nonselective method of ionization such as field ionization or electron impact, 2) analysis of a relatively crude fraction using GC or batch sample introduction with selective ionization and/or chemical derivatization methods designed to enhance detection of the compound types of interest, and 3) GC/MS analysis of targeted components, which may be chemically derivatized to enhance detection or improve their GC characteristics. Early work relied almost exclusively on the first approach because of limitations in MS instrumentation. The others have received more attention in recent literature because of the considerable time savings achieved and their suitability for more routine applications. Representative examples of the latter two approaches were cited at the beginning of this section. The primary focus of this review is on the first approach, since it has accounted for the bulk of the existing knowledge of acidic compounds (e.g., table 1), and is the most applicable to this work.

Carboxylic acids present a considerable challenge for MS because of their tendency to adsorb onto glass and metal surfaces, decarboxylate upon heating, and fragment extensively after ionization. Also, both aliphatic and aromatic structures are typically present. In their classic work, Seifert and coworkers circumvented these problems by initially reducing pure carboxylic acid concentrates to alcohols using LiAlH_4 , followed by tosylation and further reduction of the tosylate esters to hydrocarbons (17-20). Since separation and MS methods for hydrocarbons were relatively well developed by that time, analysis of the resulting hydrocarbons was straightforward. Subsequent attempts at direct analysis of carboxylic acid concentrates have relied on field (22) and chemical (30) ionization techniques in order to minimize fragmentation. In addition, prior esterification or silylation enhances their

volatility and greatly reduces losses from adsorption during analysis. Although direct analysis of carboxylic acids, or their esters/silyl derivatives, prevents potential loss from more complex chemical transformations such as those of Seifert et al., only low resolution spectra are attainable with the present instrumentation in the appropriate ionization modes (e.g., field, chemical, or fast atom bombardment). Thus, for identification of sulfur-containing or other carboxylic acid subclasses requiring high MS resolving power, the only feasible approach is one analogous to that of Seifert et al.

MS analysis of aromatic acidic classes is inherently simpler because of their suitability for analysis by low voltage electron impact MS (LV/EI/MS), a well established MS technique, and the relatively unrestricted applicability of other MS modes. High resolution LV/EI/MS may also be used to detect multiple heteroatom-containing compounds, e.g., amides or difunctional acids.

In MS analysis of aromatic types, the main challenge is establishing the functionalities and other structural features of the species detected. This has principally been done through chemical separations and independent functional group assessments discussed earlier. However, further confirmation and additional structural information have been obtained in recent work through chemical derivatization and advanced instrumental techniques.

For example, Appendix 4 describes MS analysis of ArOH as their trifluoroacetate esters. After acylation, ArOH are readily differentiated from other single oxygen types and Ar(OH)₂ are easily distinguished from carboxylic acids and other O₂-types. In addition, comprehensive GC/MS analysis of lower boiling ArOH concentrates is greatly facilitated by the improved GC resolution and more characteristic mass spectra obtained after acylation. Zanella et al. employed silylation for similar purposes in their analyses of ArOH (118). Alternately, Wood et al. used MS/MS to differentiate ArOH in coal liquid by neutral loss (H₂O) scanning and examination of daughter spectra (119). Also, chemical ionization with methanol and deuterated methanol may be used to differentiate between ArOH and aromatic ethers/alcohols (120). GC/IR/MS could conceivably be used to confirm functionality of MS homologs, but thus far has been applied only to simple mixtures of ArOH and carboxylate esters (121).

Differentiation of acidic versus basic nitrogen compounds has largely been based on chemical separations because few methods exist for independent assessment of nitrogen functionalities in a given fraction. However, chemical ionization MS may be used to distinguish between primary, secondary, and tertiary forms of nitrogen (122). In petroleum, secondary versus tertiary nitrogen would indicate pyrrolic versus pyridinic homologs, respectively. Also, the methylation procedure described in Appendix 2 appears to provide quantitative conversion of pyrrolic compounds, and thus would potentially be useful in their differentiation from basic species in MS analysis. Dorbon et al. employed N-methylation in conjunction with GC/MS analysis of carbazoles and benzocarbazoles (37,39). In this work, the ability to distinguish types of nitrogen was needed in order to evaluate the effectiveness of chromatographic separations in the course of their development. In addition, this capability is essential in the analysis of multiheteroatomic compounds to determine if the acidic group is based on nitrogen and/or other heteroatoms present.

No general methods for MS analysis of thiols or other predominantly saturated acidic classes were found from searching the literature. In both early (56) and recent (123) work, the relatively few known thiols have been identified by individual comparisons with authentic standards. Problems with analysis of thiols include many of those listed earlier for carboxylic acids, in addition to their ready conversion to disulfides in the presence of air. The recent identification of 9-*n*-alkyl fluorene-9-ols in Athabasca bitumen (22,31) dispels conventional wisdom that petroleum does not contain alcohols. The difficulties in MS analysis of alcohols, similar to those of thiols, may explain their lack of detection in earlier analyses.

Gas chromatography is the primary technique used for analysis of individual acidic compounds. In the case of low boiling fractions of relatively simple composition, GC and/or GC/MS can provide a comprehensive analysis of selected acidic classes. However, a more typical application is determination of preselected components which constitute a minor portion of the overall sample. The GC characteristics of alkylphenols and some higher ArOH have been determined on several types of GC columns (124-133). Virtually all the columns investigated contained highly specialized liquid phase coatings designed to minimize peak asymmetry and provide maximum resolution of

isomers. Also, most exhibited relatively low upper temperature limits which effectively restricted their use to low boiling ArOH. These disadvantages prompted development of the derivatization approach discussed in Appendix 4, which employs commonly available methylsilicone columns. The retention indices of carbazole, the methylcarbazoles, and selected di-, tri- and tetramethylcarbazoles, the benzocarbazoles and selected dibenzocarbazoles have been determined on low polarity GC columns (134,135). As the result, these compounds have been identified in several petroleum and syncrude fractions (37-40,69,136).

The primary value of individual compound analysis is in elucidation of specific geochemical or chemical parameters or effects. For example, the biological origin of selected carboxylic acids was established via identification of specific biomarker compounds, as discussed earlier. Recognition of this fact in turn allows for assignment of more realistic structures to homologous series detected in group-type MS analyses. For example, a series with empirical formula $C_nH_{2n-8}O_2$ is consistent with either a benzoic acid or tricyclic terpenoid-based structure. Prior knowledge clearly favors the latter possibility. Similarly, GC analysis for geometric isomers typically reveals relative abundances that reflect thermodynamic stability, probability of formation from a given precursor, or other factors. For example, previously cited work has shown a predominance of carbazole over other benzindole isomers, and a predominance of nonlinear configurations of higher benzologs (e.g., benzo[a]carbazole ~ benzo[c]carbazole >> benzo[b]-carbazole), which corresponds to analogous cases for other compound types (e.g., phenanthrene >>anthracene, benzo[h]quinoline >> acridine). Again, this information significantly augments information from more general analyses and improves the overall understanding of petroleum composition. When coordinated with refining processes, effects of steric hindrance, aromaticity and other structural factors can be determined from detailed analysis. For example, o-alkylation increased the resistance of phenols to hydrodeoxygenation (137) while 1-methylcarbazole decreased more than less hindered alkylcarbazole isomers during hydrotreating (39). Also, benzocarbazoles were more reactive than carbazole homologs (39,42). Finally, unequivocal identification of one or more members of a compound class or subclass is normally part of the process of establishing its presence in petroleum.

Overall Assessment

A significant amount is known about the structure and chemistry of acidic compounds in lower boiling ranges of petroleum, but not those from high boiling or nondistillable fractions. Determination of general parameters, such as total acidity, as well as analyses for preselected compounds or classes may be performed with little or no prior separation. However, a more comprehensive analysis requires separation of acids from other types followed by further fractionation into compound classes. Apparatus, materials, and techniques employed in most prior separations of acids are largely obsolete due to the development of HPLC technology. Many of the key instrumental methods of analysis, including MS, require supporting information from separation chemistry, chemical derivatization or other types of sample modification, and/or complementary techniques for adequate data interpretation.

The obsolescence of existing procedures for separating acidic classes and inherent difficulties in adapting them to HPLC instrumentation prompted development of the TMAH-silica method described in this report. However, preliminary evaluations of HPLC columns with various mobile phases indicated that appreciable overlap of acidic compound classes, resulting primarily from steric effects, could occur even under optimum conditions. Thus, analysis of fractions obtained from actual petroleums and synfuels is needed to assess the actual severity of class overlap, and to provide a basis for developing schemes capable of compensating for incomplete separation. For expediency, fractions from previously characterized petroleums and synfuels are more suitable for this purpose than those from Cerro Negro, owing to the greater complexity and unknown character of the latter.

The need for new analysis methods largely arose from problems encountered in development of separations and evaluation of the resulting fractions. For example, analysis of very weakly acidic and multifunctional acids was largely overlooked in prior work.

Based on preliminary results in Chapter 2, both the relatively high percentage of acidic compounds containing two or more heteroatoms in Cerro Negro (excluding O_2 -compounds; 12 and 23 wt % of the 200-425° C and 425-550° C total acids, respectively) plus its overall high degree of isomeric complexity will require maximum performance from the best available separation and

instrumental techniques even to obtain a satisfactory analysis of distillable acids. Only rudimentary analyses can be performed on nondistillable acids with present methodology.

EXPERIMENTAL

Detailed procedures for specialized methods used in the analysis of whole acid concentrates and subfractions appear in the appendices at the end of this chapter. This section largely describes conditions for subfractionation of whole acid concentrates isolated via NIE procedures discussed earlier in Chapter 2. Modifications in the procedure initially used for acid subfractionations, through the course of its development to the present version, are described to facilitate comparison of results obtained with early versus later separations. Also, optimization of separation conditions and practical aspects of performing separations are discussed.

HPLC Conditions for Distillate Acid Fractions

Table 6 lists conditions initially employed for subfractionating acid concentrates from Cerro Negro and other petroleum distillates. The construction and procedure for packing silica columns were identical to that described in Chapter 2 for columns used in saturate/neutral-aromatic separations. Solvents used as eluents were of high purity grade. TMAH was purchased from Aldrich (Milwaukee, WI) as a 20% solution in methanol. Repetitive separations (0.3 g per injection) were typically performed in order to subfractionate up to 5 g of a given acid concentrate.

Gradient optimization and determination of fraction cutpoints were largely based on the behavior of a blend of pure compounds listed in table 7. A representative chromatogram of the standard blend obtained under these conditions is shown in figure 4, along with a corresponding chromatogram obtained from separation of a Cerro Negro 200-425° C acid concentrate. Segments of the chromatograms corresponding to subfractions 1-6 are noted in the figure.

TABLE 6. - HPLC conditions for distillable acids, ca. 1982-1984

HPLC:	Spectra Physics (San Jose, CA) Model 8000
Column dimensions:	30 cm x 2.5 cm (I.D.) 316 ss
Column packing:	10 μ m SiO ₂ (Adsorbosil-LC, Alltech Associates, Deerfield, IL).
N, average plates/m:	15,000-20,000
Flow rate, mL/min:	28
Chart speed, cm/min:	0.5 cm/min
Temperature, ° C:	35.0 $\pm$ 0.1°C
UV detector:	ISCO (Lincoln, NE) UA-5, 1 mm path cell, 280 nm, 0-2 AUFS
Injection vol, mL:	1.8
Injection amount, mg:	300
Gradient:	Linear

Time, min	Volume percent		
	A	B	C
0	88	12	0
2	88	12	0
17	78	22	0
30	20	80	0
38	20	80	0
50	0	30	70
51	0	30	70
53	88	12	0
65	88	12	0

A: Methyl t-butyl ether (MTBE).

B: 70 percent (v/v) MTBE, 30 percent (v/v) methanol (MeOH), 0.03 percent (w/v) tetramethylammonium hydroxide (TMAH).

C: MeOH with 0.015 percent (w/v) TMAH.

Fraction collection timing

Fraction No.	Anticipated Class	Time Interval (min)	
		A. Initial	B. Modified
1	Neutral contaminants	0-6.8	0-6.3
2	Pyrrolic benzologs	6.8-17.1	6.3-15.0
3	Amides	17.1-19.8	15.0-20.0
4	ArOH	19.8-35.5	20.0-33.0
5	RCOOH	35.5-44.5	33.0-43.0
6	Bifunctional acids	44.5-60.0	43.0-60.0

FIGURE 4. - Preparative scale HPLC chromatograms of the standard blend (A, see table 7) and a Cerro Negro 200-425°C acid concentrate (NIE Run 2). See table 6 for experimental conditions. Regions 1-6 correspond to cutpoints specified in table 6, "A"-series.

IR and elemental analysis of fractions from the separation of 200-425° C acids shown in figure 4 as well as 425-550° C and 550-700° C Cerro Negro acids led to the modified fraction cutpoints (B) indicated in table 6. The cutpoint between subfractions 2 and 3 was advanced from 17.1 (initial) to 15.0 minutes because hydroxyl compounds, presumably ArOH, were detected in addition to pyrrolic benzologs in subfraction 2. Subfraction 3, initially anticipated to contain amides due to its correspondence with the elution of oxindole in the standard, was found to contain pyrrolic benzologs, ArOH, and carbonyl compounds which may or may not have been amides. The other fractions largely contained the classes designated in table 6, to the extent discernible from the limited analytical data available. Thus, with the modified cutpoints, the range of subfraction 3 was expanded to cover the region of apparent overlap between pyrrolic benzologs and ArOH.

TABLE 7. - Compounds in the ca. 1982-1987 acid standard blend

Peak Number	Compound
1	Dibenzofuran
2	Benzophenone
3	13H-Dibenzo[a,i]carbazole
4	Oxindole
5	2,4,5-Trimethylphenol
6	o-Cresol
7	3,4-Dimethylphenol
8	Phenol
9	2-Naphthol
10	1-Fluorene-carboxylic acid
11	p-Toluic acid
12	2,2-Diphenylpropanoic acid
13	1-Naphthoic acid

The conditions in table 6 (B. cutpoints) were extensively applied in separation of over 20 acid concentrates from Cerro Negro and Wilmington petroleum distillates, in addition to acids from an SRC-II coal liquid and an OSCR in-situ retorted shale oil (137). In the case of Cerro Negro acids, the driving force behind re-separation was not the minor modification in cutpoints, but rather the availability of acid fractions from an improved version of the NIE procedure. Initial subfractionations were largely performed on acids from

the first NIE separations (Run 1 - see Appendix 2, Chapter 2). The second set of subfractionations was performed on the more representative acid fractions discussed in the main body of Chapter 2.

Subsequent evaluation of fractions from the above separations (see Results and Discussion) pointed out the need for further optimization of the HPLC procedure. For example, the isocratic segment in table 6 between 30 and 38 min was found to provide incomplete resolution of ArOH and carboxylic acids. A second generation solvent program incorporating a longer run time and other modifications was subsequently developed (see ref. 138, table 3). However, resolution between pyrrolic benzologs and ArOH in Wilmington 650-1000° F acids remained inadequate even after those changes (138).

A concurrent detailed study of tetraalkylammonium hydroxide-silica HPLC systems revealed an inherent limitation in their use for petroleum acid subfractionation (102). Increasing the TMAH or other tetraalkylammonium hydroxide concentration improved resolution of pyrrolic benzologs and ArOH at the expense of the separation between ArOH and carboxylic acids, and vice versa. Thus, the optimum experimental conditions attainable reflect a compromise between resolution of those classes.

Figure 5 illustrates this offsetting effect of TMAH concentration on resolution of compounds in the standard blend in table 7. In this case, resolution of pyrrolic benzologs and ArOH may be approximated as the difference in retention time (Δ_1) of 13H-dibenzo[a,i]carbazole (peak 3) versus 2,4,5-trimethylphenol (peak 5); resolution of ArOH and carboxylic acids is reflected by the difference in retention (Δ_2) of 2-naphthol (peak 9) and 1-fluorenicarboxylic acid (peak 10). 2,4,5-Trimethylphenol elutes well ahead of phenol (peak 8) because of the combined steric and inductive effects of the methyl groups, which lower its acidity as discussed in the Introduction. Similarly, 2-naphthol elutes after phenol because the additional aromatic ring increases its acidity relative to phenol. As shown by comparison of figures 5A versus 5B, doubling the TMAH concentration, while holding other variables constant, increases Δ_1 from 4.0 to 7.0 minutes while decreasing Δ_2 from 12.4 to 8.8 minutes. Changing the gradient profile (figure 5C) in order to decrease retention of all ArOH to approximately the same as that observed with 0.01% TMAH (figure 5A) yields only a minor improvement in Δ_2 (9.0 min) over figure 5B, while decreasing Δ_1 significantly over that attained in figure 5B.

FIGURE 5. - HPLC chromatograms of the standard blend (table 7) as a function of TMAH concentration (A vs. B) and gradient profile (B vs. C). Δ_1 and Δ_2 indicate the difference in retention between components 3/5 and 9/10, respectively. Retention times (min) are specified for each component. See text.

Since the potential improvement in resolution of acidic classes from variation of either eluent composition and/or gradient profiles is limited by the above effect, the remaining options for reducing class overlap consist largely of increasing 1) column efficiency (number of theoretical plates), and/or 2) run time. The conditions in table 8 reflect increases in both of these parameters for the current version of the method. The separation of the standard blend shown in figure 5B was obtained using conditions specified in table 8. Also, separation of Cerro Negro 200-425° C acids attained with those conditions is shown in figure 6. Although a detailed discussion of separations obtained in figures 4B versus 6 is deferred to the Results and Discussion section, visual comparison of the chromatograms reveals the significantly improved resolution obtained with the current conditions.

As part of the development of the method, silicas from several suppliers were evaluated for their ability to resolve acidic classes. Aside from differences attributable to physical properties such as particle size and surface area, their performance was quite similar. This observation is consistent with the prior conclusion that separation selectivity is primarily controlled by interaction of acids with silica-bound and free TMAH (102). In general, slightly different experimental conditions were required for the various silica columns in order to obtain equivalent separations of the standard blend (table 7) and/or other test samples. However, some adjustment of conditions is typically required even to obtain equivalent results from columns supplied from the same vendor.

TABLE 8. - Current HPLC conditions for distillable acids

HPLC:	Spectra Physics Model 8000
Column:	DYNAMAX SiO ₂ (Rainin Instr. Co., Woburn, MA) 25 cm x 21.4 mm (I.D.) Two 25 cm columns are connected in series.
Column packing:	Rainin 8 μ m irregular silica.
N, average plates/m:	>40,000 (specified by Rainin)
Flow rate, mL/min:	25
Chart speed, cm/min:	0.5
Temperature, ° C:	35.0 $\pm$ 0.1
UV detector:	ISCO UA-5, 1 mm path cell, 280 nm, 0-2 AUFS
Injection vol, mL:	1.8
Injection amount, mg:	300
Gradient:	Linear

Time, min	Volume percent		
	A	B	C
0	95	5	0
2	95	5	0
5	91	9	0
30	88	12	0
60	0	100	0
70	0	50	50
75	0	50	50
78	95	5	0
86	95	5	0

A: Methyl t-butyl ether (MTBE).

B: 70 percent (v/v) MTBE, 30 percent (v/v) methanol (MeOH), 0.02 percent (w/v) tetramethylammonium hydroxide (TMAH).

C: MeOH with 0.02 percent (w/v) TMAH.

Fraction collection timing

<u>Fraction No.</u>	<u>Anticipated Class</u>	<u>Time Interval¹ (min)</u>
1	Very weak acids	0-9
2	Hindered pyrrolic benzologs	9-14
3	Pyrrolic benzologs	14-28
4	ArOH	28-50
5	RCOOH	50-68
6	Difunctional acids	68-86

¹Typical.

FIGURE 6. - HPLC chromatogram of Cerro Negro 200-425°C acids (NIE Run 4) obtained using current conditions (table 8). Compare with figure 4B.

At the present, separation selectivity is best defined in terms of the retention of key compounds in a standard blend of pure compounds or other type of test sample. Retention times of the standard serve as reference points for 1) detecting changes in selectivity over the lifetime of a given column or recognizing mechanical or other types of problems during daily operation, 2) fraction cutpoints, 3) assessing changes in selectivity obtained with different columns or experimental conditions, and 4) optimization of experimental conditions. Slight shifts in retention (<1 min) of standard components were usually compensated for by corresponding adjustment of fraction cutpoints. TMAH concentration and/or the gradient profile were adjusted as required to maintain consistent separation factors (e.g., Δ_1 and Δ_2 in figure 5) between standard compounds. Thus, it should be recognized that conditions specified in tables 6 and 8 are nominal, and that the most relevant means of defining "separation conditions" are the actual chromatograms of the standard blend such as those in figures 4A and 5. As discussed in Chapter 4, a similar approach was used to define selectivity for subfractionation of bases.

As discussed earlier, optimization of the mobile phase for a given column largely consists of determining the concentration of TMAH which provides the desired compromise between resolution of pyrrolic benzologs/ArOH and ArOH/carboxylic acids. However, resolution between these groups is also affected by the gradient profile, which is essentially the rate of change in the methyl t-butyl ether (MTBE)/methanol (MeOH) ratio. Slowing the gradient profile over the regions near the beginning and end of elution of ArOH will improve their resolution from pyrrolic benzologs and carboxylic acids, respectively. For example, the concentration of "B" eluent is changed only 3 percent in the gradient segment from 5 to 30 minutes under current conditions (table 8) in order to maximize resolution of pyrrolic benzologs versus ArOH. However, only limited improvement in resolution of acidic classes is practically achievable through this approach, even at the expense of greatly increased run time.

The increased resolution of weakly acidic compounds effected by current versus early experimental conditions may be seen by comparing the portions of the chromatograms of Cerro Negro 200-425° C acids (figures 6 versus 4B), corresponding approximately to subfractions 1-3 in each case. The greatly

enhanced retention of pyrrolic benzologs (subfractions 2 and 3) relative to unretained compounds (subfraction 1) in figure 6 reflects the lower initial concentration of "B" eluent and slower gradient profile in current use. Since the original standard blend did not contain any compounds eluting between the unretained components (dibenzofuran and benzophenone) and 13H-dibenzo[a,i]carbazole, it has subsequently been modified to include two compounds eluting in that region--2,3-dimethylindole and 2,6-dimethylphenol. In addition, two redundant carboxylic acids were deleted and a difunctional acid was added. Table 9 lists compounds in the current standard.

TABLE 9. - Compounds in the current acid standard blend

Peak Number	Compound
1	Dibenzofuran
2	Benzophenone
3	2,3-Dimethylindole
4	2,6-Dimethylphenol
5	Oxindole
6	13H-Dibenzo[a,i]carbazole
7	2,4,5-Trimethylphenol
8	o-Cresol
9	3,4-Dimethylphenol
10	Phenol
11	2-Naphthol
12	1-Fluorene-carboxylic acid
13	1-Naphthoic acid
14	4-Hydroxybenzoic acid

Methanolic solutions of TMAH are mildly corrosive to stainless steel; thus, columns and instrumental components which contact the mobile phase were flushed with MTBE after use.

New silica columns require preconditioning with TMAH in order to obtain repeatable separations under gradient conditions. Although this may be accomplished by simply programming the instrument to run several gradient cycles through a new column, the preconditioning process can be accelerated significantly by first pumping about ten column volumes of a 0.2:99.8 TMAH:MeOH solution through the column.

Separation repeatability is improved through continuous cycling of the gradient program through the column as opposed to intermittent use. Thus, fully automated instrumentation, including fraction collection, is highly desirable for this application, since it can perform repetitive separations under a precisely controlled time sequence. After significant periods of inactivity (e.g., overnight), the instrument should be allowed to run through one gradient cycle before resuming actual separations.

HPLC Conditions for Acid Fractions from Distillation Residues or Whole Crudes

The mediocre solubility of nondistillable acid fractions in the mobile phase described in the previous section limits its application to acids from distillates only. Although the approach and methodology used for subfractionating nondistillable acids are basically the same as for those from distillates, the major mobile phase component is chloroform rather than MTBE. While chloroform has significant disadvantages compared to MTBE, including higher toxicity and a negative impact on column life, it dissolves acid fractions from whole crudes or distillation residues extremely well. Table 10 summarizes conditions for the chloroform-based HPLC system.

The chloroform-based separation has undergone little change since its initial development because the available methods for analysis of the resulting subfractions from petroleum resids were incapable of obtaining the level of detail required for optimization of the procedure, or even if optimization was needed. Conditions in table 10 were selected in order to obtain separations of the standard blend which matched those from the MTBE-based procedure in table 6 as closely as possible. However, resolution of ArOH and carboxylic acids is inherently poorer with the chloroform-based mobile phase (102). The TMAH concentration in the mobile phase is kept relatively low in order to compensate for this inadequacy, which in turn decreases the resolution attainable between ArOH and pyrrolic benzologs. The instrumentation, approach, and steps taken in calibrating and carrying out separations are the same as described for the MTBE-based system.

TABLE 10. - HPLC conditions for subfractionation of nondistillable acids

HPLC:	Spectra Physics Model 8000
Column dimensions:	30 cm x 2.5 cm (I.D.) 316 ss
Column packing:	10 μ m SiO ₂ (Adsorbosil-LC, Alltech Associates, Deerfield, IL).
N, average plates/m:	15,000-20,000
Flow rate, mL/min:	30
Chart speed, cm/min:	0.5
Temperature, °C:	30.0 $\pm$ 0.1°C
UV detector:	ISCO UA-5, 1 mm path cell, 280 nm, 0-2 AUFS
Injection vol, mL:	1.8
Injection amount, mg:	300
Gradient:	Linear

Time, min	Volume percent		
	A	B	C
0	70	30	0
2	70	30	0
12	0	99	1
37	0	85	15
50	0	50	50
51	0	50	50
52	0	100	0
54	70	30	0
67	70	30	0

A: n-hexane

B: 95 percent (v/v) chloroform, 5 percent (v/v) ethanol

C: Methanol containing 0.005 percent (w/v) tetramethylammonium hydroxide

Fraction collection timing

<u>Fraction No.</u>	<u>Anticipated Class</u>	<u>Time interval (min)</u>
1	Neutral contaminants/very weak acids	0-7.0
2	Pyrrolic benzologs	7.1-16.0
3	Pyrrolic benzologs/hindered ArOH	16.1-20.0
4	ArOH	20.1-34.0
5	RCOOH/multifunctional acids	34.1-58.0

During development of the procedure, acid fractions from selected distillates were subfractionated under conditions nominally specified in table 10 in order to compare composition of subfractions from the two mobile phase systems. However, given the significant disadvantages of the chloroform-based system listed above, along with shorter column life, subsequent application of this system has been limited to acid fractions where its use was essential for solubility reasons.

Removal of TMAH From Subfractions

Quantitative removal of TMAH from subfractions is essential to obtain separation mass balances and to convert acids present as TMAH salts back to their free acid form prior to analysis. TMAH removal was initially performed via simple aqueous extraction as described below.

TMAH extraction was performed after the bulk of the solvent had been removed by rotary evaporation. Benzene was added to dilute the subfraction to approximately 50 mL, and 25 mL of an aqueous solution 1 M in HCl and NaCl was added. The mixture was magnetically stirred for ca. 30 min and the aqueous and organic layers were separated in a separatory funnel. The above was repeated; then, the aqueous extracts were combined, back extracted with 20 mL of benzene, and discarded. The original benzene solution containing the subfraction was combined with the 20 mL benzene used for back extraction of the aqueous solution and extracted a final time with deionized water to remove any residual HCl or NaCl. The organic layer was dried over anhydrous sodium sulfate and the benzene was evaporated under nitrogen. Fractions containing relatively volatile components (<300° C) were incompletely evaporated and the residual benzene was determined by GC as described in Chapter 2 for whole acid concentrates. Higher boiling fractions were taken to constant weight.

The above procedure worked reasonably well on most petroleum-derived subfractions, except those containing predominantly carboxylic acids and those exhibiting appreciable water solubility (i.e., from low boiling distillates). For both of the latter, significant losses occurred from aqueous emulsion and dissolution. The surfactant properties of the tetramethylammonium ion aggravated the normal tendency of carboxylic acids to form emulsions and may have increased losses from aqueous dissolution. Various organic and inorganic salts were added to the aqueous solution in an attempt to suppress these effects, but these efforts were largely

unsuccessful. In addition, the extraction procedure generally performed poorly on subfractions from either coal liquids or shale oils, typically accounting for losses of up to 20% of the total acids separated.

Alternates to the aqueous extraction examined include the following: precipitation of TMAH with CO_2 and SO_2 , and removal via adsorption onto silica bonded with carboxyl or sulfonic acid groups, and thermal decomposition to volatile products. Also, several adsorbents designed to selectively retain subfraction components while allowing for elution of TMAH were evaluated. Recovery of pure compounds and actual petroleum fractions, as well as the degree of TMAH removal attained, were the major criteria in judging the success of each procedure. However, practical aspects such as speed and convenience were also considered. In the final assessment, none of the above performed significantly better than aqueous extraction. However, a recently developed method for TMAH removal, based on an acrylic type weakly acidic cation exchange resin, has performed well during its initial evaluation and subsequent applications. It is described below.

The adsorbent, BioRex 70 200-400 mesh cation exchange resin (BioRad, Richmond, CA), is prepared for use as follows. One kg resin is placed in a large Buchner funnel and washed with 12 L 2 M HCl, deionized water to a neutral pH, followed by 12 L MeOH. The resin is then transferred to a large Soxhlet apparatus, where it is extracted with MeOH overnight. The prepared resin is stored under MeOH until use. A given subfraction is prepared for TMAH removal by dissolution in 2 mL 1:1 MeOH:toluene, which is then transferred to a 1.5 cm i.d. glass column containing a 3-5 cm bed of prepared resin. The subfraction components are eluted with 10-20 mL MeOH, depending on visual assessment of the quantity required for complete elution. Treated subfractions are filtered through 0.5 μm teflon filters and taken to dryness--or near dryness in the case of fractions containing relatively volatile components as discussed earlier.

Analysis of Subfractions

Elemental analysis of subfractions was performed in the manner described in Chapter 1 for whole distillates and crudes. Infrared spectra were obtained and interpreted as described in Appendix 1, in conjunction with information on N-H band characteristics supplied in Chapter 2. Functional group analysis by NMR was initially performed via reaction with bis(tri-n-butyltin) oxide and

quantitation of the ^{119}Sn signal at chemical shifts corresponding to ArOH and carboxyl derivatives (139). However, this procedure was ultimately abandoned in favor of the one described in Appendix 2 because of nonquantitative yields of derivatives obtained with carboxyl and particularly N-H functional groups. Nonaqueous titration (NAT) for determination of equivalent weight and the ratio of strong versus weak acids was carried out according to the procedure in Appendix 3. In addition, methodology and instrumentation described in Chapter 5A for recording synchronized scanning fluorescence spectra of aromatic hydrocarbon fractions were used here to obtain spectra of acid subfractions.

The current conditions for GC/MS analyses of ArOH as their trifluoroacetate esters are described in Appendix 4. However, analyses of ArOH prior to ca. 1987 utilized a different acylation procedure and GC conditions. These are described in detail elsewhere (103), but GC/MS conditions are reprinted in table 11A for the reader's convenience. Conditions for GC/MS analysis of other classes were essentially identical to those used for ArOH. The procedure for formation of methyl esters of carboxylic acids prior to GC or GC/MS analysis was described earlier (28). Silylation of ArOH and carboxylic acids (103) was employed in very early GC and GC/MS analyses.

Qualitative GC determinations of distributions of N- and S-containing compounds relative to the total species present in a given subfraction were performed on a chromatograph fitted with flame ionization (total), flame photometric (sulfur) and thermionic (nitrogen) detectors. The column effluent was equally divided among the detectors using a zero dead volume union with a three-hole ferrule and appropriate lengths of deactivated fused silica tubing. Make-up gas (He) was used to increase the flow through each detector to 30 mL/min. Other conditions were as specified in table 11B.

A preliminary evaluation of microprobe sample introduction for high resolution MS (HR/MS) analysis of subfractions exhibiting low volatility was carried out as described in Appendix 5. By necessity, the bulk of the effort was actually spent toward developing computer software for data acquisition and subsequent calculation of the results shown in the appendix. Batch introduction HRMS analysis of subfractions was performed in the same manner described in Chapter 2 for whole acid fractions.

TABLE 11. - Summary of GC and GC/MS analysis conditions

A. GC/MS

Instrument:	Kratos (Ramsey, NJ) MS-80 GC/MS with Carlo Erba Model 4662 GC, and Data General Nova-4-based DS-55 data system
Injector:	Split/splitless, 300° C
Interface:	Direct, 300° C
MS Conditions:	70 eV ionization voltage, 1,000 dynamic resolution, 0.5 sec/decade scan rate, 5×10^{-6} source pressure, 300° C source temperature
GC Conditions:	0.25 mm x 30 m, 0.25 μ m film thickness, J and W (Rancho Cordova, CA) DB-5 column. Temperature program: 50° C (hold one min), 5° C/min to 350° C (hold 20 min).
He Flow Rate:	1 mL/min.

B. GC - Three-way Detection

Instrument:	Perkin-Elmer (Norwalk, CT) Sigma 2 GC with flame ionization, flame photometric and thermionic detectors, and IBM AT-based P-E-Nelson Analytical data system
Injector:	On column, 300° C
Detector Temperature:	320° C (all)
Column:	0.53 mm x 30 m, 1.5 μ m film thickness, J and W DB-5
Temperature Program:	70° C (zero hold), 5° C/min to 300° C (hold 10 min).
He flow rate:	30 mL/min

RESULTS AND DISCUSSION

Separation and analysis of strong and weak acid concentrates from an SRC-II coal liquid are discussed in the first section because, although much of the work was performed with prototype versions of the various methods, those results define separation behavior of key acidic classes to a level of detail not attainable from work on petroleum fractions. The simpler composition of coal-derived syncrude versus petroleum accounts for the higher level of detail obtainable from analysis of SRC-II subfractions.

The second section describes separation and analysis of a Wilmington 370-535° C acid concentrate composited from several repetitive NIE separations. Most of this work was done with current versions of the separation and analytical methods; thus, this section demonstrates the degree of separation and analysis attainable with present methodology.

The third section compares subfractionation results for acid concentrates obtained with various versions of the NIE procedure. These results underscore the dependence of findings from subsequent subfractionation and analysis on the method employed for initial isolation of total acids.

The fourth section provides a summary of available data on composition of Cerro Negro acids and a comparison with analogous results from other petroleums.

Separation and Analysis of SRC-II >325° C Strong and Weak Acid Concentrates

A coal liquid sample obtained from a 1977 run of the Solvent Refined Coal (SRC-II) pilot plant operated at Fort Lewis, WA, was extensively employed in development of analytical methods for this and other chapters. The composition of this sample shows an intermediate degree of complexity which, combined with a relatively low distillation endpoint (<500° C), makes it an ideal test sample. A more detailed description and other research applications of this material may be found elsewhere ([140](#),[141](#)). Separation and analysis of acid subfractions from the portion of SRC-II boiling above 325° C were performed in order to obtain a better understanding of the chemistry of the NIE and HPLC methods, and to assess their performance in isolating and resolving acidic compound classes.

Table 12 shows mass balances from the initial NIE separation as well as from subfractionation of the strong and weak acid concentrates. The fully optimized version of the NIE method (see Chapter 2) was used in this case; the essentially quantitative mass and nitrogen balances obtained and the low level of nitrogen in the neutral fraction indicate satisfactory performance of the procedure. Subfractionation of strong and weak acid concentrates was performed under earlier conditions specified in table 6; TMAH was removed from the resulting subfractions via aqueous extraction. The low recovery of strong acids (84 wt %) can largely be attributed to losses during extraction of TMAH, as noted in the Experimental Section. Extraction of TMAH from weak acid subfractions proceeded smoothly, owing to their hydrophobic nature and lower average acidity.

Representative HPLC chromatograms of each acid concentrate and the standard are shown in figure 7. The distinctly different distribution of acidic types in the strong versus weak concentrates is quite apparent in the figure. Representative structures shown for classes in strong and weak acid subfractions are based on results from GC/MS and IR analysis.

In general, the elution behavior of compounds in the SRC-II acid concentrates paralleled that of the standard blend quite well. For example, for weak acids the dominant components in subfraction 1 were aromatic hydrocarbons and other species expected to exhibit minimal retention such as that shown by dibenzofuran and benzophenone in the standard. Similarly, the dominant class in subfraction 2 from the weak acid concentrate was pyrrolic benzologs, primarily carbazole and benzo[a]carbazole homologs which elute before dibenzo[a,i]carbazole in the standard. Weak acid subfraction 3 contained nearly equal proportions of pyrrolic benzologs and ArOH, in agreement with the corresponding elution of representative members of each class present in the standard. Benzo[c]carbazole overlapped into subfraction 4A because the cutpoint between subfractions 3/4A occurred virtually at the apex of its elution; otherwise, subfraction 4A contained primarily ArOH. The dominant class in strong acid subfractions 2-4 was ArOH, the bulk of which eluted into subfraction 4 in accordance with the majority of ArOH in the standard blend. SRC-II does not contain significant levels of carboxylic acids; however, Ar(OH)₂ types present eluted at approximately the same or somewhat later times than carboxylic acids in the standard.

TABLE 12. - Mass balances from separation of SRC-II >325° C¹

A. Nonaqueous Ion Exchange (NIE)

<u>Fraction</u>	<u>Yield (Wt % >325° C)</u>	<u>Elemental N Content (Wt % Fraction)</u>	<u>H/C (Atomic Ratio)</u>
Strong acids	18.0	0.98	0.964
Weak acids	12.9	3.87	0.955
Strong bases ²	13.5	5.58	0.923
Weak bases	1.36	3.25	0.884
Neutrals	54.7	0.04	0.892
Balance	100.5	1.50	0.921
Whole >325° C	-	1.58	0.920

B. Subfractionation of Weak Acids

<u>Subfraction</u>	<u>Yield Wt % Weak Acids</u>	<u>Wt % Total Acids</u>
1	8.2	3.4
2	60	25
3	15	6.3
4A	14	5.8
4B	3.2	1.3
5	2.6	1.1
Total	103	43

C. Subfractionation of Strong Acids

<u>Subfraction</u>	<u>Yield Wt % Strong Acids</u>	<u>Wt % Total Acids</u>
1	1.3	0.8
2	3.2	1.9
3	5.0	2.9
4	62	36
5	12	7.0
Total	84	49

¹Obtained from redistillation of recombined middle (75.5 wt %) and heavy (24.5 wt %) distillates obtained from Fort Lewis Pilot Run 77SR-12. Yield of >325° C boiling range was 16.0 wt %.

²Discussed in Chapter 4.

FIGURE 7. - HPLC chromatograms of SRC-II >325°C strong and weak acid concentrates compared to that of the standard blend (table 7). Conditions as specified in table 6 ("B"-series cutpoints). See table 12 for subfraction yields.

The most negative finding from this analysis was that the degree of overlap between ArOH and pyrrolic benzologs was greater than expected. Hydroxyl compounds, presumably ArOH, were identified by GC/MS even in subfraction 2 from the strong acids and were also detected later by IR in the weak acid subfraction 2. As noted above, elution of selected pyrrolic benzologs in the weak acid concentrate occurred as late as subfraction 4A. The approximate extent of overlap between these classes may be visualized by mentally superimposing the figure 7 chromatograms for weak and strong acids and noting the regions where they coincide. Awareness of this problem intensified ongoing efforts toward optimization of separation conditions.

For comparison, figures 8 and 9 show chromatograms of weak and strong acids separated using current conditions in table 8. The degree of resolution of ArOH obtained in the initial separation of weak acids (figure 7, subfraction 4A) is noticeably improved in figure 8, as is the resolution between pyrrolic benzologs (subfraction 2) and aromatic hydrocarbons in subfraction 1. However, coelution of relatively aromatic pyrrolic benzologs and hindered ArOH still occurs under current conditions, as evidenced by the approximately equal retention times of benzo[c]carbazole in the weak acid fraction versus 2,4,5-trimethylphenol in the standard. Similarly, while the chromatogram of the strong acid fraction in figure 9 shows decreased (compared with figure 7) levels of ArOH in regions where elution of pyrrolic benzologs normally occurs, approximately 2.2 wt % of the total strong acids still exhibit equal or lower retention than the standard compound dibenzo[a,i]carbazole, even under current experimental conditions. As discussed below, the comparable elution times of selected ArOH and pyrrolic benzologs reflect both steric and inductive effects causing their retention to be decreased and enhanced, respectively, relative to the bulk of the species in their class.

The increased combined yield of $\text{Ar}(\text{OH})_2$ types in subfractions 4 and 5 from the more recent subfractionation of strong acids (20.5 wt %, see figure 9) is significantly greater than obtained initially for total $\text{Ar}(\text{OH})_2$ in subfraction 5 (12 wt %, see table 12C). The discrepancy indicates that a significant proportion of the unrecovered material in the original separation was $\text{Ar}(\text{OH})_2$ compounds.

FIGURE 8. - HPLC separation of SRC-II >325°C weak acids compared to that of the current standard (table 9) using current conditions (table 8). Note the improved resolution between subfractions 1/2 and 3/4 over that obtained in figure 7.

FIGURE 9. - HPLC separations of SRC-II >325°C strong acids and the standard blend in table 7. Conditions as specified in table 8. Note the overall increase in retention of ArOH (major peak) compared to figure 7 and the decreased proportion of early eluting material (2.2 wt %). See text.

Perhaps the most surprising finding was the significant improvement afforded in the overall resolution of acidic classes by the preliminary NIE separation into strong and weak acid types. Subfractionation of total (strong + weak) acids would clearly have resulted in greater overlap of pyrrolic benzologs and ArOH, for example. As discussed in Chapter 4, NIE prefractionation of strong versus weak bases significantly improved their subfractionation and analysis as well.

Tables 13-15 summarize results from IR and GC/MS* analysis of subfractions from the initial HPLC separations (table 12, figure 7). GC/MS conditions were those specified in table 11A in the Experimental Section. Each subfraction was analyzed neat and after acylation and/or silylation as described earlier (103). Comparison of GC/MS results on underivatized versus derivatized samples was employed for confirmation of structural assignments based in part on library mass spectra supplied with the instrument's data system, published GC retention indices and supporting data (48,62,134-136,142), and reference GC retention data and mass spectra generated in-house (e.g., see Appendix 4). Quantitation was typically based on relative total ion current (TIC) peak area, although in some cases sample complexity forced use of selected ion (usually molecular ion) intensities for estimation of relative amounts present. Relative TIC response is generally as reliable as flame ionization detector (FID) response for GC quantitation. For example, figure 10 compares GC/MS (TIC) versus GC/FID chromatograms of the whole weak acid concentrate. Relative peak areas from the two chromatograms were in good agreement, typically within $\pm 10\%$ $((A_{TIC} - A_{FID})/A_{TIC} \times 100\%)$ for major components. The uniform response of the FID is widely recognized.

*Strong acid subfraction 5 was analyzed by probe microdistillation HR/MS as described in Appendix 5.

FIGURE 10. - Comparison of GC/MS total ion current (TIC) and GC/FID chromatograms of whole SRC-II >325°C weak acids (table 14F). GC/MS conditions were as specified in table 11A; conditions for the GC/FID chromatogram were similar, except that a different instrument and slower temperature program (4°C/min) were used. Note the similarity in TIC vs. FID relative response.

Detailed interpretation of data summarized in tables 13-15 provided considerable insight into separation behavior of acidic compounds over both the NIE and HPLC subfractionation steps. However, in many cases, the existing library of GC and MS information was inadequate for complete elucidation of potentially significant effects, since the exact--or sometimes even general--structures of compounds occurring in various subfractions often could not be determined. Also, the analytical techniques themselves were not adequate for determination of all types present. Thus, the diversity of types, classes and/or homologs present in most subfractions is undoubtedly greater than reflected in the tables. Nevertheless, since it is recognized that the scant 20-or-so pages of data which were decipherable from the analysis could still overwhelm even the dedicated reader, an attempt to further summarize and present salient conclusions is made below.

TABLE 13. - Infrared analysis of SRC-II >325° C acid subfractions

Subfraction	-----Compound Types, wt %-----			
	OH ¹	NH ²	C=O ³	Total
A. Weak Acids				
1	6.6	11	- ⁴	18
2	8.5(12) ⁵	90	- ⁴	99
3	49	67	- ⁴	116
4A	78	22	9	109
4B	() ⁶	() ⁶	14	-
5	() ⁶	() ⁶	13	-
Balance ⁷	24	68	2	94
Whole	29	62	3.9	95
B. Strong Acids				
1	ND ⁸	ND	29	29
2	28 ⁶ (31) ⁵	() ⁶	20	51
3	53 ⁶	() ⁶	25	78
4	72 ⁶ (72) ⁵	() ⁶	6	78
5	incomplete dissolution			-
Whole	Not available			-

¹⁻³ ϵ 's used in calculations were 143, 179, and 580 Lm⁻¹cm⁻¹, respectively.

⁴Small C=O band indicating phthalate impurity (1720 cm⁻¹).

⁵Determined after acylation with CF₃C(O)Cl (ϵ =606).

⁶Very broad hydrogen-bonded OH/NH band observed.

⁷Calculated from data for individual subfractions.

⁸None detected.

TABLE 14. - Results from GC/MS analysis of SRC-II 325° C+ whole weak acids and subfractions

A. SUBFRACTION 1.

Z-series	Compound or Homolog	MW	Wt % (Subfraction Basis)	Wt % Weak Acids	Wt % Total Acids
-18H	Alkylphenanthrenes/anthracenes (10 isomers)	192-220	0.4	0.03	0.01
-22H	Fluoranthene	202	0.3	0.02	0.01
	Benzofluorene(s) ¹	216	39.8	3.3	1.4
	C ₁ -benzofluorenes (2 isomers)	230	18.1	1.5	0.6
	C ₂ -benzofluorenes (4 isomers)	244	2.8	0.2	0.1
	Total benzofluorenes	-	60.7	5.0	2.1
	Total -22H	-	61.0	5.0	2.1
-24H	9-Phenylfluorene	242	1.4	0.1	0.05
	C ₁ -9-phenylfluorene (2 isomers)	256	2.6	0.2	0.1
	C ₂ -9-phenylfluorene (3 isomers)	270	3.1	0.3	0.1
	C ₃ -9-phenylfluorene (2 isomers)	284	0.3	0.02	0.01
	Total 9-phenylfluorenes	-	7.4	0.6	0.3
	Other phenylfluorene isomer	242	8.5	0.7	0.3
	C ₁ -homolog	256	3.5	0.3	0.1
	Total phenylfluorenes	-	19.4	1.6	0.7
-28H	Dibenzofluorenes (2 isomers)	266	4.1	0.3	0.1
	C ₁ -dibenzofluorenes (4 isomers)	280	2.0	0.2	0.07
	Total dibenzofluorenes	-	6.1	0.5	0.2

¹Tentatively identified as benzol[*a*]fluorene, but other isomers may also be present.

A. SUBFRACTION 1 (continued).

Z-series	Compound or Homolog	MW	Wt % (Subfraction Basis)	Wt % Weak Acids	Wt % Total Acids
-32H	Phenylbenzofluorenes (3 isomers)	292	2.2	0.2	0.1
	C ₁ -homologs (2 isomers)	306	0.2	0.02	0.01
	Total phenylbenzofluorenes	-	2.4	0.2	0.1
-15N	Carbazole	167	0.1	0.01	0.003
	C ₁ -carbazoles (4 isomers)	181	0.2	0.02	0.007
	C ₂ -carbazoles (1 isomer)	195	0.04	-	-
	Total carbazoles	-	0.3	0.03	0.01
-23N	Nonpyrrolic nitrogen type(s)				
	C ₀ -(3 isomers)	257	4.8	0.4	0.2
	C ₁ -(7 isomers)	271	3.5	0.3	0.1
	C ₂ -(4 isomers)	285	1.4	0.1	0.05
	C ₃ -(2 isomers)	299	0.3	0.02	0.01
	Total -23N	-	10.0	0.8	0.3
	SUMMARY				
-18+/-32H	Total hydrocarbons	233 ¹	89.3	7.3	3.1
-15N	Total pyrrolic benzologs	-	0.3	0.03	0.01
-23N	Total other nitrogen types	267 ²	10.0	0.8	0.3
	TOTAL	235 ³	99.6	8.1	3.4

¹ Average for hydrocarbons.

² Average for nitrogen compounds.

³ Average for whole subfraction.

B. SUBFRACTION 2.

Z-series	Compound or Homolog	MW	Wt % (Subfraction Basis)	Wt % Weak Acids	Wt % Total Acids
-15N	Carbazole	167	13.3	8.0	3.3
	1-methylcarbazole	181	6.8	4.1	1.7
	3-methylcarbazole	181	7.4	4.4	1.9
	2-methylcarbazole	181	8.0	4.8	2.0
	4-methylcarbazole	181	4.2	2.5	1.0
	Total C ₁ -carbazoles	-	26.4	15.8	6.6
	C ₂ -carbazoles (13 isomers)	195	22.6	13.6	5.7
	C ₃ -carbazoles (15 isomers)	209	11.1	6.7	2.8
	C ₄ -carbazoles (15 isomers)	223	6.5	3.9	1.6
	C ₅ -carbazoles (8 isomers)	237	1.2	0.7	0.3
	C ₆ -carbazoles (2 isomers)	251	0.1	0.06	0.03
	Total carbazole homologs (C ₀ -C ₆)	-	81.2	48.7	20.3
	Benz(g)indole	167	0.2	0.1	0.05
	C ₁ -benz(g)indole	181	0.7	0.4	0.2
	Total benz(g)indole homologs (C ₀ -C ₁)	-	0.9	0.5	0.2
	Total -15N	-	82.1	49.2	20.5
-17N	Naphthenocarbazoles/ naphthenobenzindoles				
	C ₀ -5 member ring (4 isomers)	207	2.3	1.4	0.6
	C ₁ -5 member ring (8 isomers)	221	2.8	1.7	0.7
	C ₀ -6 member ring (3 isomers)	221	1.5	0.9	0.4
	C ₂ -5/C ₁ -6 member rings (3 isomers)	235	0.3	0.2	0.1
	C ₃ -5/C ₂ -6 member rings (1 isomer)	249	0.04	0.02	0.01
	Total 5-member ring	-	5.1	3.1	1.3
	Total 6-member ring	-	1.5	0.9	0.4
	Total -17N	-	7.0	4.2	1.8

B. SUBFRACTION 2 (continued).

Z-series	Compound or Homolog	MW	Wt % (Subfraction Basis)	Wt % Weak Acids	Wt % Total Acids
-19N	Dinaphthenocarbazoles	219	0.2	0.1	0.05
-21N	Benzo[a]carbazole	217	2.5	1.5	0.6
	Benzo[b]carbazole	217	0.8	0.5	0.2
	Total C ₀ -benzocarbazoles	217	3.3	2.0	0.8
	C ₁ -benzocarbazoles (6 isomers)	231	2.3	1.4	0.6
	C ₂ -benzocarbazoles (6 isomers)	245	1.1	0.7	0.3
	C ₃ -benzocarbazoles (3 isomers)	259	0.6	0.3	0.1
	Total -21N	-	7.3	4.4	1.8
-23N	Phenylcarbazoles/ naphthenobenzocarbazoles				
	C ₀ -(2 isomers)	243	0.7	0.4	0.2
	C ₁ -(6 isomers)	257	0.7	0.4	0.2
	C ₂ -(3 isomers)	271	0.3	0.2	0.1
	Total -23N	-	1.7	1.0	0.4
SUMMARY					
-15+--23N	Total pyrrolic benzologs	197 ¹	98.3	59	24.6
-22,-24H	Benzofluorene and other hydrocarbons	216	1.7	1.0	0.4
	TOTAL	198 ²	100.0	60	25

¹ Average for pyrrolic benzologs.

² Average for whole subfraction.

C. SUBFRACTION 3.

Z-series	Compound or Homolog	MW	Wt % (Subfraction Basis)	Wt % Weak Acids	Wt % Total Acids
-15N	Carbazole	167	1.6	0.2	0.1
	Benz(g)indole	167	2.1	0.3	0.1
	Benz(e)indole	167	5.6	0.8	0.4
	C ₁ -benzindoles (10 isomers)	181	9.5	1.4	0.6
	C ₂ -benzindoles (4 isomers)	195	0.8	0.1	0.05
	Total -15N	-	19.6	2.9	1.2
-17N	2-Phenylindole/ naphthenobenzindoles				
	C ₀ -(1 isomer)	193	1.9	0.3	0.1
	C ₁ -(2 isomers)	207	1.2	0.2	0.1
	Total -17N	-	3.1	0.5	0.2
-21N	Benzo[a]carbazole	217	3.1	0.5	0.2
	Benzo[b]carbazole	217	1.5	0.2	0.1
	Benzo[c]carbazole	217	15.4	2.3	1.0
	Total benzocarbazoles	-	20.0	3.0	1.3
	C ₁ -benzocarbazoles (5 isomers)	231	11.5	1.7	0.7
	C ₂ -benzocarbazoles (3 isomers)	245	3.4	0.5	0.2
	C ₃ -benzocarbazoles (3 isomers)	259	0.8	0.1	0.05
	C ₄ -benzocarbazoles (1 isomer)	273	0.1	0.02	0.01
	Dibenzoindole	217	0.4	0.06	0.03
	Total -21N	-	36.2	5.4	2.3
-23N	Phenylcarbazoles/ naphthenobenzocarbazoles				
	C ₀ (3 isomers)	243	1.6	0.2	0.1
	Total -23N	243	1.6	0.2	0.1

C. SUBFRACTION 3 (continued).

Z-series	Compound or Homolog	MW	Wt % (Subfraction Basis)	Wt % Weak Acids	Wt % Total Acids
-25N	Fluorenoindole/etc.				
	C ₀ -(1 isomer)	255	0.1	0.02	0.01
	C ₁ -(1 isomer)	269	0.1	0.02	0.01
	Total -25N	-	0.2	0.03	0.01
-27N	Dibenzocarbazoles (3 isomers)	267	0.4	0.06	0.03
-6(0)	Alkylphenols	234-248	0.2	0.03	0.01
-8(0)	Alkylcyclohexyl/naphthenophenols	218-260	4.8	0.7	0.3
-10(0)	Dinaphthenophenols	202-258	5.4	0.8	0.3
-12(0)	Trinaphthenophenols	214-270	6.6	1.0	0.4
-14(0)	Alkylphenylphenols/etc.	226-282	9.3	1.4	0.6
-16(0)	Alkylphenylindanols/etc.	238-294	10.8	1.6	0.7
-18(0)	Naphtheno -16(0) compounds	264-292	1.9	0.3	0.1
<u>SUMMARY</u>					
-15→-27N	Total pyrrolic benzologs	209 ¹	61	9.1	3.9
-6→-16(0)	Total ArOH	246 ²	39	5.9	2.4
	TOTAL	223 ³	100	15.0	6.3

¹ Average for pyrrolic benzologs.

² Average for ArOH.

³ Average for whole subfraction.

D. SUBFRACTION 4A.

Z-series	Compound or Homolog	MW	Wt % (Subfraction Basis)	Wt % Weak Acids	Wt % Total Acids
-15N	Benzindoles	167-181	3.7	0.5	0.2
-21N	Benzo[c]carbazole	217	14.6	2.0	0.8
	Dibenzoindole	217	2.8	0.4	0.2
	C ₁ -homolog	231	1.3	0.2	0.1
	Total -21N	-	18.7	2.6	1.1
-25N	Fluorenoindole/etc. (1 isomer)	269	0.3	0.04	0.02
-27N	Dibenzocarbazole (1 isomer)	267	1.7	0.2	0.1
-8(0)	Alkylcyclohexyl/naphthenophenols	218-260	3.3	0.5	0.2
-10(0)	Dinaphthenophenols	216-244	3.0	0.4	0.2
-12(0)	Trinaphthenophenols	214-242	3.2	0.4	0.2
-14(0)	Alkylphenylphenols/etc.	240-296	7.5	1.0	0.4
-16(0)	Alkylphenylindanols/etc.	224-308	21.4	3.0	1.3
-18(0)	Naphtheno -16(0) compounds	250-320	6.5	0.9	0.4
-20(0)	Alkylphenylnaphthols/etc.	248-332	16.0	2.2	0.9
-22(0)	Unknown ArOH	274-344	9.1	1.3	0.5
-24(0)	Unknown ArOH	272-342	5.6	0.8	0.3
SUMMARY					
-15+--27N	Total pyrrolic benzolgs	215 ¹	24.4	3.4	1.4
-8+--24(0)	Total ArOH	288 ²	75.6	10.6	4.4
	TOTAL	271³	100.0	14.0	5.8

¹ Average for pyrrolic benzolgs.

² Average for ArOH.

³ Average for whole subfraction.

E. SUMMATION OF SUBFRACTIONS 1-4A.

Z-series	Compound or Homolog	MW	Wt % Weak Acids	Wt % Total Acids
-18H	Alkylphenanthrenes/anthracenes (10 isomers)	192-220	0.03	0.01
-22H	Fluoranthene	202	0.02	0.01
	Benzofluorene(s) ¹	216	4.3	1.8
	C ₁ -benzofluorenes (2 isomers)	230	1.5	0.6
	C ₂ -benzofluorenes (4 isomers)	244	0.2	0.1
	Total -22H	-	6.0	2.7
-24H	Phenylfluorenes (2 isomers)	242	0.8	0.4
	C ₁ -phenylfluorenes (3 isomers)	256	0.5	0.2
	C ₂ -phenylfluorenes (3 isomers)	270	0.3	0.1
	C ₃ -phenylfluorenes (2 isomers)	284	0.02	0.01
	Total -24H	-	1.6	0.7
-28H	Dibenzofluorenes (2 isomers)	266	0.3	0.1
	C ₁ -dibenzofluorenes (4 isomers)	280	0.2	0.07
	Total -28H	-	0.5	0.2
-32H	Phenylbenzofluorenes (3 isomers)	292	0.2	0.1
	C ₁ -homologs (2 isomers)	306	0.02	0.01
	Total -32H	-	0.2	0.1
-15N	Carbazole	167	8.2	3.4
	1-methylcarbazole	181	4.1	1.7
	3-methylcarbazole	181	4.4	1.9
	2-methylcarbazole	181	4.8	2.0
	4-methylcarbazole	181	2.5	1.0
	Total C₁-carbazoles	-	15.8	6.6

¹Tentatively identified as benzo[a]fluorene, but other isomers may also be present.

E. SUMMATION OF SUBFRACTIONS 1-4A (continued).

Z-series	Compound or Homolog	MW	Wt %	Wt %
			Weak Acids	Total Acids
-15N (cont)	C ₂ -carbazoles (13 isomers)	195	13.6	5.7
	C ₃ -carbazoles (15 isomers)	209	6.7	2.8
	C ₄ -carbazoles (15 isomers)	223	3.9	1.6
	C ₅ -carbazoles (8 isomers)	237	0.7	0.3
	C ₆ -carbazoles (2 isomers)	251	0.06	0.03
	Total carbazole homologs (C ₀ -C ₆)	-	49.0	20.4
	Benz(g)indole	167	0.4	0.2
	Benz(e)indole	167	1.0	0.4
	C ₁ -benzindoles (11 isomers)	181	2.1	0.9
	C ₂ -benzindoles (4 isomers)	195	0.1	0.04
	Total benzindole homologs (C ₀ -C ₂)	-	3.6	1.5
	Total -15N	-	52.6	21.9
-17N	Naphthenobenzindole/ 2-phenylindole (1 isomer)	193	0.3	0.1
	Naphthenocarbazoles/ naphthenobenzindoles			
	C ₀ -5 member ring (4 isomers)	207	1.6	0.6
	C ₁ -5 member ring (8 isomers)	221	1.7	0.7
	C ₀ -6 member ring (3 isomers)	221	0.9	0.4
	C ₂ -5/C ₁ -6 member rings (3 isomers)	235	0.2	0.1
	C ₃ -5/C ₂ -6 member rings (1 isomer)	249	0.02	0.01
	Total -17N	-	4.4	1.8
-19N	Dinaphthenocarbazoles	219	0.1	0.05

E. SUMMATION OF SUBFRACTIONS 1-4A (continued).

Z-series	Compound or Homolog	MW	Wt % Weak Acids	Wt % Total Acids
-21N	Benzo[a]carbazole	217	2.0	0.8
	Benzo[b]carbazole	217	0.7	0.3
	Benzo[c]carbazole	217	4.3	1.8
	Total C ₀ -benzocarbazoles	-	7.0	2.9
	Dibenzindoles (2 isomers)	217	0.8	0.3
	C ₁ -homologs	231	3.3	1.4
	C ₂ -homologs	245	1.2	0.5
	C ₃ -homologs	259	0.4	0.2
	C ₄ -homologs	273	0.02	0.01
	Total -21N	-	12.7	5.3
-23N	Phenylcarbazoles/ naphthenobenzocarbazoles			
	C ₀ -homologs	243	0.6	0.2
	C ₁ -homologs	257	0.4	0.2
	C ₂ -homologs	271	0.2	0.1
	Nonpyrrolic types (subfraction 1)	257-299	0.8	0.3
	Total -23N	-	2.0	0.8
-25N	Fluorenoindoles/etc.			
	Total -25N	255-269	0.07	0.03
-27N	Dibenzocarbazoles	267	0.3	0.1
-6(0)	Alkylphenols	234-248	0.03	0.01
-8(0)	Alkylcyclohexyl/naphthenophenols	218-260	1.2	0.5
-10(0)	Dinaphthenophenols	202-258	1.2	0.5
-12(0)	Trinaphthenophenols	214-270	1.4	0.6
-14(0)	Alkylphenylphenols/etc.	226-296	2.4	1.0

E. SUMMATION OF SUBFRACTIONS 1-4A (continued).

Z-series	Compound or Homolog	MW	Wt % Weak Acids	Wt % Total Acids
-16(0)	Alkylphenylindanols/etc.	224-308	4.6	1.9
-18(0)	Naphtheno -16(0) compounds	250-320	1.2	0.5
-20(0)	Alkylphenylnaphthois/etc.	248-332	2.2	0.9
-22(0)	Unknown ArOH	274-344	1.3	0.5
-24(0)	Unknown ArOH	272-342	0.8	0.3
<u>SUMMARY</u>				
	Total hydrocarbons	233 ²	8.3	3.5
	Total nonpyrrolic nitrogen types	267 ²	0.8	0.3
	Total pyrrolic benzologs	200 ²	71.4	29.8
	Total ArOH	275 ²	16.4	6.8
	TOTAL	216 ³	96.9	40.4
	Gravimetric weight from subfractionation	-	97.2	40.6

²Average for specified type.

³Average for whole weak acid fraction.

F. DIRECT ANALYSIS OF WHOLE WEAK ACIDS.

Z-series	Compound or Homolog	• MW	Wt % Weak Acids		Wt % Total Acids (Corrected)
			Uncorrected	Corrected	
-22H	Benzofluorene (1 isomer)	216	5.8	4.6	1.9
	C ₁ -benzofluorenes (3 isomers)	230	2.4	1.9	0.8
	C ₂ -benzofluorenes (1 isomer)	244	0.1	0.1	0.04
	Total -22H	-	8.3	6.6	2.8
-24H	Phenylfluorene (1 isomer)	242	0.1	0.1	0.04
	C ₁ -phenylfluorenes (2 isomers)	256	0.2	0.2	0.1
	C ₂ -phenylfluorenes (2 isomers)	270	0.3	0.2	0.1
	Total -24H	-	0.6	0.5	0.3
-28H	Dibenzofluorene (1 isomer)	266	0.2	0.2	0.1
-15N	Carbazole + benz(g)indole	167	13.6	10.9	4.5
	1-methylcarbazole	181	5.2	4.2	1.8
	3-methylcarbazole	181	9.3	7.4	3.1
	2-methylcarbazole	181	6.2	5.0	2.1
	4-methylcarbazole	181	3.0	2.4	1.0
	Total C ₁ -carbazoles	-	23.7	19.0	8.0
	C ₂ -carbazoles (13 isomers)	195	14.2	11.4	4.7
	C ₃ -carbazoles (13 isomers)	209	6.9	5.5	2.3
	C ₄ -carbazoles (10 isomers)	223	4.0	3.2	1.3
	C ₅ -carbazoles (2 isomers)	237	0.4	0.3	0.1
	C ₆ -carbazoles (1 isomer)	251	0.3	0.2	0.1
	Total carbazole homologs (C ₀ -C ₆)	-	63.1	50.5	21.1
	Benz(e)indole	167	0.8	0.6	0.3
	C ₁ -benzindole	181	0.7	0.6	0.3
	Total benzindole homologs (C ₀ -C ₁)	-	1.5	1.2	0.6
	Total -15N	-	64.6	51.7	21.7

F. DIRECT ANALYSIS OF WHOLE WEAK ACIDS (continued).

Z-series	Compound or Homolog	MW	Wt % Weak Acids		Wt % Total Acids (Corrected)
			Uncorrected	Corrected	
-17N	Naphthenocarbazoles/ naphthenobenzindoles				
	C ₀ -5 member ring (4 isomers)	207	2.6	2.1	0.9
	C ₁ -5/C ₀ -6 member ring (6 isomers)	221	2.7	2.2	0.9
	C ₂ -5/C ₁ -6 member ring (1 isomer)	235	0.1	0.1	0.04
	Total -17N	-	5.4	4.3	1.8
-21N	Benzo(a)carbazole	217	3.8	3.0	1.3
	Benzo(b)carbazole	217	0.3	0.2	0.1
	Benzo(c)carbazole	217	6.0	4.8	2.0
	Total C₀-benzocarbazoles	-	10.1	8.0	3.4
	C ₁ -benzocarbazoles (7 isomers)	231	5.2	4.2	1.8
	C ₂ -benzocarbazoles (4 isomers)	245	1.8	1.4	0.6
	C ₃ -benzocarbazoles (2 isomers)	259	0.3	0.2	0.1
	C ₄ -benzocarbazoles (1 isomer)	273	0.2	0.2	0.1
	Total 21N	-	17.6	14.0	5.9
-23N	Phenylcarbazoles/ naphthenobenzocarbazoles				
	C ₀ -(2 isomers)	243	1.3	1.0	0.4
	C ₁ -(4 isomers)	257	0.8	0.6	0.3
	C ₂ -(2 isomers)	271	0.4	0.3	0.1
	C ₃ -(2 isomers)	285	0.2	0.2	0.1
	Total -23N	-	2.7	2.1	0.9
	SUMMARY				
	Total hydrocarbons	218 ¹	9.1	7.3	3.1
	Total pyrrolic benzologs	196 ²	90.3	72.1	30.2
	Total ArOH	-	- ⁴	16.4	6.8
	TOTAL	198 ³	99.4	95.8	40.1

¹ Average for pyrrolic benzologs

² Average for ArOH

³ Average for whole fraction

⁴ No ArOH were detected in the direct analysis of whole weak acids.

G. PARTITIONING OF COMPOUNDS OVER SUBFRACTIONS 1-4A.

Z-series	Compound Type or Homolog	Subfraction	MW	Wt % Weak Acids	Wt % Total Acids	Relative Proportion (%)
-18+32H	Hydrocarbons	1	192-306	7.3	3.1	88
		2	-	1.0	0.4	12
	Total hydrocarbons	-	-	8.3	3.5	100
-15N	Carbazole + alkylcarbazoles	1	167-181	0.03	0.01	0.06
		2	167-251	48.7	20.3	99.6
		3	167	0.2	0.1	0.4
	Total carbazoles	-	-	48.9	20.4	100
	Benz(g)indole	2	167	0.1	0.05	25
		3	167	0.3	0.1	75
	Total benz(g)indole	-	-	0.4	0.2	100
	Benz(e)indole	3	167	0.8	0.4	100
	Alkylbenzindoles	2	181	0.4	0.2	17
		3	181-195	1.5	0.6	62
		4A	167-181	0.5	0.2	21
	Total alkylbenzindoles	-	-	2.4	1.0	100
	Cumulative -15N	1	-	0.03	0.01	0.06
		2	-	49.2	20.5	93.5
		3	-	2.8	1.2	5.3
		4A	-	0.5	0.2	1.1
	Total -15N	-	-	52.6	21.9	100
-17N	Naphtheno-15N	2	207-249	4.2	1.8	89
		3	193-207	0.5	0.2	11
	Total -17N	-	-	4.7	2.0	100
-19N	Dinaphtheno-15N	2	219	0.1	0.05	100
-21N	Benzo[a]carbazole	2	217	1.5	0.6	75
		3	217	0.5	0.2	25
	Total benzo[a]carbazole	-	-	2.0	0.8	100

G. PARTITIONING OF COMPOUNDS OVER SUBFRACTIONS 1-4A (continued).

Z-series	Compound Type or Homolog	Subfraction	MW	Wt % Weak Acids	Wt % Total Acids	Relative Proportion (%)
-21N (cont)	Benzo(b)carbazole	2	217	0.5	0.2	71
		3	217	0.2	0.1	29
	Total benzo(b)carbazole	-	-	0.7	0.3	100
	Benzo(c)carbazole	3	217	2.3	1.0	53
		4A	217	2.0	0.8	47
	Total benzo(c)carbazole	-	-	4.3	1.8	100
	Dibenzindoles	3	217	0.06	0.03	12
		4A	217	0.4	0.2	88
	Total dibenzindoles	-	-	0.5	0.2	100
	C ₁ -C ₄ -homologs	2	231-259	2.4	1.0	49
		3	231-273	2.3	1.0	47
		4A	231	0.2	0.1	4
	Total C₁-C₄-homologs	-	-	4.9	2.1	100
	Cumulative -21N	2	-	4.4	1.8	35
		3	-	5.5	2.3	43
		4A	-	2.6	1.1	22
	Total -21N	-	-	12.7	5.2	100
-23N	Nonpyrrolic types	1	257-299	0.8	0.3	40
	Phenylcarbazoles/ naphthenobenzocarbazoles	2	243-271	1.0	0.4	50
		3	243	0.2	0.1	10
	Total -23N	-	-	2.0	0.8	100
-25N	Fluorenoindole/etc.	3	255-269	0.03	0.01	43
		4A	269	0.04	0.02	57
	Total -25N	-	-	0.07	0.03	100

G. PARTITIONING OF COMPOUNDS OVER SUBFRACTIONS 1-4A (continued).

Z-series	Compound Type or Homolog	Subfraction	MW	Wt % Weak Acids	Wt % Total Acids	Relative Proportion (%)
-27N	Dibenzocarbazoles	3	267	0.06	0.03	20
		4A	267	0.2	0.1	80
	Total -27N	-	-	0.3	0.1	100
-6(0)	Alkylphenols	3	234-248	0.03	0.01	100
-8(0)	Alkylcyclohexyl/naphthenophenols	3	218-260	0.7	0.3	58
		4A	218-260	0.5	0.2	42
	Total -8(0)	-	-	1.2	0.5	100
-10(0)	Dinaphthenophenols	3	202-258	0.8	0.3	67
		4A	216-244	0.4	0.2	33
	Total -10(0)	-	-	1.2	0.5	100
-12(0)	Trinaphthenophenols	3	214-270	1.0	0.4	71
		4A	214-242	0.4	0.2	29
	Total -12(0)	-	-	1.4	0.6	100
-14(0)	Alkylphenylphenols/etc.	3	226-282	1.4	0.6	58
		4A	240-296	1.0	0.4	42
	Total -14(0)	-	-	2.4	1.0	100
-16(0)	Alkylphenylindanols/etc.	3	238-294	1.6	0.7	44
		4A	224-308	3.0	1.3	56
	Total -16(0)	-	-	3.6	2.0	100
-18(0)	Naphtheno-16(0) compounds	3	264-292	0.3	0.1	25
		4A	250-320	0.9	0.4	75
	Total -18(0)	-	-	1.2	0.5	100
-20+-24(0)	ArOH	4A	248-342	4.3	1.7	100

G. PARTITIONING OF COMPOUNDS OVER SUBFRACTIONS 1-4A (continued).

Z-series	Compound Type or Homolog	Subfraction	MW	Wt % Weak Acids	Wt % Total Acids	Relative Proportion (%)
<u>SUMMARY</u>						
-18+-32H	Hydrocarbons	1	233 ¹	7.3	3.1	88
		2	-	1.0	0.4	12
	TOTAL	-	233 ²	8.3	3.5	100
-23N	Nonpyrrolic nitrogen types	1	267 ¹	0.8	0.3	100
-15+-27N	Pyrrolic benzologs	1	-	0.03	0.01	0.04
		2	197 ¹	59	24.6	82
		3	209 ¹	9.1	3.9	13
		4A	215 ¹	3.4	1.4	5
	TOTAL	-	200 ²	71.5	29.9	100
-6+-24(0)	ArOH	3	246 ¹	5.9	2.4	36
		4A	288 ¹	10.6	4.4	64
	TOTAL	-	275 ²	16.5	6.8	100

¹ Average for subfraction.

² Average for whole weak acids.

TABLE 15. - Results from GC/MS analysis of SRC 11-325° C+ strong acid subfractions

A. SUBFRACTION 2.

Z-series	Compound or Homolog	MW	Wt % (Subfraction Basis)	Wt % Strong Acids	Wt % Total Acids
-10(0)	Unknown OH				
	C ₀ -(1 isomer)	202	2.0	0.06	0.04
	C ₁ -(1 isomer)	216	1.6	0.05	0.03
	Total -10(0)	-	3.6	0.1	0.07
-16(0)	Unknown OH				
	C ₀ -(1 isomer)	196	1.5	0.05	0.03
	C ₁ -(4 isomers)	210	6.0	0.2	0.1
	C ₂ -(7 isomers)	224	6.2	0.2	0.1
	C ₃ -(5 isomers)	238	5.3	0.2	0.1
	C ₄ -(1 isomer)	252	1.5	0.05	0.03
	Total -16(0)	-	20.5	0.7	0.4
-20(0)	Unknown OH				
	C ₀ -(2 isomers)	234	12.0	0.4	0.2
	C ₁ -(6 isomers)	248	11.5	0.4	0.2
	C ₂ -(4 isomers)	262	5.1	0.2	0.1
	Total -20(0)	-	28.6	0.9	0.5
-22(0)	Unknown OH				
	C ₀ -(1 isomer)	246	1.0	0.06	0.03
	C ₁ -(4 isomers)	260	4.8	0.2	0.1
	C ₂ -(5 isomers)	274	4.8	0.2	0.1
	C ₃ -(3 isomers)	288	1.9	0.06	0.03
	Total -22(0)	-	13.3	0.4	0.2
-24(0)	Unknown OH				
	C ₀ -(2 isomers)	272	1.5	0.05	0.03
	C ₂ -(1 isomer)	286	1.0	0.03	0.02
	Total -24(0)	-	2.5	0.08	0.05

A. SUBFRACTION 2 (continued).

Z-series	Compound or Homolog	MW	Wt % (Subfraction Basis)	Wt % Strong Acids	Wt % Total Acids
<u>SUMMARY</u>					
-10+-24(0)	Total hydroxyl compounds	242	68.5	2.2	1.3
-10(O ₄), -10N(O ₃), etc.	Solvent impurities and unassigned.	-	31.5	1.0	0.6

B. SUBFRACTION 3.

Z-series	Compound or Homolog	MW	Wt % (Subfraction Basis)	Wt % Strong Acids	Wt % Total Acids
-12(0)	Trinaphthenophenols	200-228	3.0	0.2	0.1
-14(0)	Alkylphenylphenols/etc. ¹				
	C ₀ -(0 isomers)	170	- ³	-	-
	C ₁ -(0 isomers)	184	-	-	-
	C ₂ -(4 isomers)	198	12.9	0.6	0.4
	C ₃ -(7 isomers)	212	15.0	0.8	0.4
	C ₄ -(6 isomers)	226	7.8	0.4	0.2
	C ₅ -(6 isomers)	240	5.5	0.3	0.2
	C ₆ -(2 isomers)	254	2.3	0.1	0.07
	Total -14(0)	-	43.5	2.2	1.4
-16(0)	Alkylfluorenols/etc. ²				
	C ₀ -(0 isomers)	182	-	-	-
	C ₁ -(1 isomers)	196	5.0	0.3	0.1
	C ₂ -(2 isomers)	210	8.0	0.4	0.2
	C ₃ -(5 isomers)	224	10.8	0.5	0.3
	C ₄ -(9 isomers)	238	13.0	0.7	0.4
	C ₅ -(9 isomers)	252	13.6	0.7	0.4
	C ₆ -(1 isomer)	266	1.3	0.07	0.04
	Total -16(0)	-	51.7	2.6	1.5
	Total ArOH	224	98.2	5.0	2.9

¹Phenylphenol, acenaphthol MW = 170; benzindanol MW = 184.

²Fluorenol MW = 182; phenylindanol MW = 210; dinaphthenonaphthol MW = 196 -224.

³Dash denotes none detected.

C. SUBFRACTION 4.

Z-series	Compound or Homolog	MW	Wt % (Subfraction Basis)	Wt % Strong Acids	Wt % Total Acids
-14(0)	Alkylphenylphenols/ benzindanols				
	C ₀ -(0 isomers)	170	-*	-	-
	C ₁ -(4 isomers)	184	10.0	6.2	3.6
	C ₂ -(9 isomers)	198	14.5	9.0	5.2
	C ₃ -(12 isomers)	212	9.0	5.6	3.3
	C ₄ -(14 isomers)	226	4.1	2.5	1.5
	C ₅ -(16 isomers)	240	1.6	1.0	0.6
	C ₆ -(6 isomers)	254	0.2	0.1	0.07
	Total -14(0)	-	39.4	24.4	14.2
-16(0)	Alkylfluorenols/ hexahydropyrenols/ phenylindanols ²				
	1-fluorenol	182	0.5	0.3	0.2
	4-fluorenol	182	2.3	1.4	0.8
	3-fluorenol	182	0.1	0.06	0.04
	2-fluorenol	182	0.7	0.4	0.3
	Total fluorenols	182	3.6	2.2	1.3
	C ₁ -fluorenols (11 isomers)	196	7.5	4.7	2.7
	C ₂ -fluorenols/etc. (14 isomers)	210	6.9	4.3	2.5
	C ₃ -fluorenols/etc. (17 isomers)	224	6.3	3.9	2.3
	C ₄ -fluorenols/etc. (11 isomers)	238	3.1	1.9	1.1
	C ₅ -fluorenols/etc. (7 isomers)	252	0.6	0.4	0.2
	C ₆ -fluorenols/etc. (2 isomers)	266	0.1	0.06	0.04
	Total -16(0)	-	28.1	17.4	10.1

¹MW phenylphenol, acenaphthol = 170; MW benzindanol = 184. Most species are phenylphenol isomers.

²MW hexahydropyrenol = 224; MW phenylindanol = 210. Most species are fluorenol isomers.

*None detected.

C. SUBFRACTION 4 (continued).

Z-series	Compound or Homolog	MW	Wt % (Subfraction Basis)	Wt % Strong Acids	Wt % Total Acids
-18(0)	Alkylphenanthrols/anthrols	194-264	3.5	2.2	1.3
-20(0)	Alkylphenylnaphthols/ dihydropyrenols				
	C ₀ -(6 isomers)	220	7.4	4.6	2.7
	C ₁ -(13 isomers)	234	9.3	5.8	3.4
	C ₂ -(14 isomers)	248	5.1	3.2	1.8
	C ₃ -(8 isomers)	262	2.1	1.3	0.8
	C ₄ -(5 isomers)	276	0.4	0.2	0.1
	Total -20(0)		24.3	15.1	8.8
-22(0)	Alkylpyrenols/benzofluorenols/ triphenylenols ³				
	pyrenols (2 isomers)	218	0.6	0.4	0.2
	C ₁ -pyrenols/C ₀ -benzo- fluorenols (10 isomers)	232	0.9	0.6	0.3
	C ₂ -pyrenols/etc. (16 isomers)	246	0.9	0.6	0.3
	C ₃ -pyrenols/etc. (14 isomers)	260	1.0	0.6	0.4
	C ₄ -pyrenols/etc. (20 isomers)	274	0.8	0.5	0.3
	C ₅ -pyrenols/etc. (12 isomers)	288	0.3	0.2	0.1
	Total -22(0)	-	4.5	2.8	1.6
-24(0)	Naphtheno-22(0)/ phenylfluorenols	244-272	0.3	0.2	0.1
	Total ArOH	215 ⁴	100	62	36

³ MW pyrenol = 218. MW benzofluorenol = 232. MW triphenylenol = 246.⁴ Average for whole subfraction.

D. SUBFRACTION 5*.

Z-series	Compound or Homolog	MW	Wt % (Subfraction Basis)	Wt % Strong Acids	Wt % Total Acids
-14(O ₂)	Dihydroxybiphenyls				
	C ₀	186	10.7	1.3	0.7
	C ₁	200	41.0	4.9	2.9
	C ₂	214	8.0	1.0	0.6
	C ₃	228	1.1	0.1	0.08
	C ₄	242	0.5	0.06	0.04
	C ₅	256	0.1	0.01	0.007
	Total -14(O₂)	-	61.4	7.4	4.3
-16(O ₂)	Dihydroxyfluorenes/ dihydroxyphenylindans ¹				
	C ₀ -DHF	198	1.4	0.2	0.1
	C ₁ -DHF	212	2.1	0.2	0.1
	C ₂ -DHF / C ₀ -DHPI	226	2.5	0.3	0.2
	C ₃ -DHF / C ₁ -DHPI	240	1.3	0.2	0.1
	C ₄ -DHF / C ₂ -DHPI	254	0.6	0.07	0.04
	C ₅ -DHF / C ₂ -DHPI	268	0.3	0.04	0.02
	Total -16(O₂)	-	8.2	1.0	0.6
-18(O ₂)	Dihydroxyphenanthrenes/ dihydroxytetrahydropyrenes/ etc. ²				
	C ₀ -DHP	210	0.7	0.08	0.05
	C ₁ -DHP	224	0.6	0.07	0.04
	C ₂ -DHP / C ₀ -DHTP	238	1.3	0.2	0.1
	C ₃ -DHP / C ₁ -DHTP	252	2.0	0.2	0.1
	C ₄ -DHP / C ₂ -DHTP	266	1.2	0.1	0.08
	C ₅ -DHP / C ₃ -DHTP	280	0.4	0.05	0.03
	C ₆ -DHP / C ₄ -DHTP	294	0.2	0.02	0.01
	Total -18(O₂)	-	6.4	0.8	0.4

*From probe microdistillation HR/MS analysis (Appendix 5).

¹MW dihydroxyfluorene = 198. MW dihydroxyphenylindans = 226.²MW dihydroxyphenanthrene = 210. MW dihydroxytetrahydropyrene = 238.

D. SUBFRACTION 5 (continued).

Z-series	Compound or Homolog	MW	Wt % (Subfraction Basis)	Wt % Strong Acids	Wt % Total Acids
-20(O ₂)	Dihydroxyphenylnaphthalenes/ dihydroxydihdropyrene/etc.	236-306	4.1	0.5	0.3
-22(O ₂)	Dihydroxypyrenes/ dihydroxybenzofluorenes/etc.	234-332	5.4	0.6	0.4
-24(O ₂)	Dihydroxychrysenes/etc.	260-344	4.0	0.5	0.3
-26(O ₂)	Dihydroxybinaphthalenes/etc.	286-356	2.3	0.3	0.2
-28(O ₂)	Dihydroxydibenzofluorenes/etc.	312-368	2.5	0.3	0.2
-30+-40(O ₂)	Ar(OH) ₂	310-442	5.7	0.7	0.4
SUMMARY					
	Total Ar(OH) ₂	231 ³	>99	>12.0	>7.0
	ArOH	-	<1	<0.1	<0.06

¹ Average for all Ar(OH)₂ present.

E. SUMMARY OF SUBFRACTIONS 2-5.

Z-series	Subfraction	MW	Wt % Strong Acids	Wt % Total Acids	Relative Proportion (%)
-10(0)	2	202-216	0.1	0.07	100
-12(0)	3	200-228	0.2	0.1	100
-14(0)	3	198-254	2.2	1.3	8
	4	184-254	24.4	14.2	92
	Total -14(0)	-	26.6	15.5	100
-16(0)	2	196-252	0.7	0.4	4
	3	196-266	2.6	1.5	15
	4	182-266	17.4	10.1	81
	Total -16(0)	-	20.7	12.0	100
-18(0)	4	194-264	2.2	1.3	100
-20(0)	2	234-262	0.9	0.5	6
	4	220-276	15.1	8.8	94
	Total -20(0)	-	16.0	9.3	100
-22(0)	2	246-288	0.4	0.2	13
	4	218-288	2.8	1.6	87
	Total -22(0)	-	3.2	1.8	100
-24(0)	2	272-286	0.08	0.05	29
	4	244-272	0.2	0.1	71
	Total -24(0)	-	0.3	0.2	100
-14(O ₂)	5	186-256	7.4	4.3	100
-16(O ₂)	5	198-268	1.0	0.6	100
-18(O ₂)	5	210-294	0.8	0.4	100
-20+40(O ₂)	5	234-442	2.8	1.7	100

E. SUMMARY OF SUBFRACTIONS 2-5 (continued).

Z-series	Subfraction	MW	Wt % Strong Acids	Wt % Total Acids	Relative Proportion (%)
<u>SUMMARY</u>					
OH-compounds	2	242 ¹	2.2	1.3	3
	3	224 ¹	5.0	2.9	7
	4	215 ¹	62	36	90
	5	-	<0.1	<0.06	100
	TOTAL	217 ²	69.0	40.1	100
(OH) ₂ -compounds	5	231 ²	12.0	7.0	100
Total (OH) _x	2-5	219 ²	81	47	-
Gravimetric weight from subfractionation	2-5	-	82	48	-

¹ Average for subfraction.

² Average for total subfractions 2-5.

Table 16 depicts partitioning of selected compounds and homologous series over the NIE and HPLC separations. The more detailed summaries of separation behavior in tables 14G and 15E may be consulted for additional information. To a large extent, the observed HPLC elution order of individual compounds and homologs within a given class reflects inductive effects on relative acidity (acidity increases with increasing aromaticity and decreases with increasing alkyl substitution) and steric effects discussed earlier in the Introduction. These factors were also responsible for the overlap in compound classes discussed above. The overall elution order of compound classes over both separations follows their relative acidity (pK_a) indicated earlier in tables 3 and 4; however, the correlation is not linear.

Specific examples of inductive effects include the increased retention of more aromatic pyrrolic benzologs (carbazole < benzo[c]carbazole < dibenzocarbazoles) and ArOH (cyclohexylphenol homologs < hydroxybiphenyl homologs). The opposite effect of alkylation is generally reflected in the typically higher initial (and average) MW observed for members of a given Z-series detected in corresponding subfractions from weak versus strong acid concentrates or lower number subfractions within either concentrate. For example, the lowest MW species in the -16(0) Z-series detected in weak acid subfractions 3 and 4A were 238 and 224, respectively (table 14G), as compared to 196, 196, and 182 for strong acid subfractions 2-4, respectively (table 15E). However, it should be noted that the carbon number (MW) distributions may also reflect other structural differences, in addition to the degree of alkylation. The broad distributions of some homologous series, including the -16(0) series cited above, attest to the overall importance of the combination of inductive and steric effects on separation behavior in both the NIE and HPLC separations.

TABLE 16. - Partitioning of selected compounds and homologs over the NIE and HPLC separations

Class	Z-Series	Structure or best available representation of structure	Fraction with highest relative abundance ¹												
			Weak acid subfractions					Strong acid subfractions							
			1	2	3	4A	4B	5	1	2	3	4	5		
"Acidic" aromatic hydrocarbons	-22H	Benzo[a]fluorene	X												
	-24H	9-phenylfluorene	X												
"Nonpyrrolic" nitrogen compounds	-23N	Phenyl-9,10-dihydro-acridine ²	X												
Pyrrolic benzologs	-15N	Carbazole homologs		X
		Benz[g]indole			X
		Benz[e]indole			X										
	-17N	Naphthenocarbazole ³		X											
	-21N	Benzo[a]carbazole		X											

¹ In cases of nearly equal abundance in more than one fraction, multiple entries are shown.² Structure consistent with available data, but actual identity unknown.³ Exact isomeric form(s) unknown.

TABLE 16.- continued

Class	Z-Series	Structure or best available representation of structure	Fraction with highest relative abundance ¹											
			Weak acid subfractions					Strong acid subfractions						
			1	2	3	4A	4B	5	1	2	3	4	5	
Pyrrolic benzologs (cont.)	21N (cont.)				X	X								
		Benzo[c]carbazole
		X								
		Naphtho[e]indole ³												
	-23N			X										
		Phenylcarbazole ³												
	-27N					X								
		Dibenzocarbazole ³												
ArOH	-8(O)				X	X								
		Cyclohexylphenol homologs ²												
	-12(O)				X									
		Octahydroxyphenol homologs ²												
	-14(O)											X		
		2-hydroxybiphenyl homologs ³												

¹ In cases of nearly equal abundance in more than one fraction, multiple entries are shown.² Structure consistent with available data, but actual identity unknown.³ Exact isomeric form(s) unknown.

TABLE 16.- continued

Class	Z-Series	Structure or best available representation of structure	Fraction with highest relative abundance ¹											
			Weak acid subfractions					Strong acid subfractions						
			1	2	3	4A	4B	5	1	2	3	4	5	
ArOH (cont.)	-14(O)												X	
		3- or 4-hydroxybiphenyl homologs ³												
	-16(O)					X						X		
		Phenylindanol homologs ²
		X	
		1-, 2-, 3-, and 4- fluorenols												
	-20(O)												X	
		Phenyl-naphthol homologs ²												
Ar(OH) ₂	-14(O ₂)												X	
		2, X'-dihydroxybiphenyl homologs												
	-14(O ₂)													X
		Phenyl-dihydroxybenzene homologs ³												
	-16(O ₂)													X
		Dihydroxyfluorene homologs ²												

¹ In cases of nearly equal abundance in more than one fraction, multiple entries are shown.² Structure consistent with available data, but actual identity unknown.³ Exact isomeric form(s) unknown.

Identification of separation behavior resulting solely from steric effects was hampered by the inability to assign specific structures to the vast majority of components detected by GC/MS. However, figures 11-13 show representative mass spectra of what may reasonably be assigned as acylated sterically hindered ArOH compounds present in subfractions 3 and 4A from the weak acid concentrate. The structures and fragmentation patterns noted in the figures are based on corresponding behavior in spectra of related standard components (Appendix 4). In figure 11, the positions of the cyclohexyl ring and alkyl groups could not be established to a sufficient degree of certainty to specify them as ortho to the hydroxyl group; but that is the most likely orientation. However, ortho substitution of phenyl and indanyl groups relative to the hydroxyl group was clearly indicated in spectra shown in figures 12 and 13, respectively, by virtue of the intense fragments corresponding to loss of CF_3 from the molecular ion. For example, acylated 2-hydroxybiphenyl is easily distinguished from other isomers by the occurrence of an intense fragment ion from loss of CF_3 (Appendix 4). Formation of cyclic intermediates analogous to those shown in the figures, possible only for ortho isomers, is the likely driving force behind the observed fragmentation pattern. This mass spectral fragmentation pattern, in addition to others indicating ortho substitution, was most prevalent in spectra of ArOH in weak acid subfractions and earlier eluting strong acid subfractions; which in turn is consistent with a higher proportion of hindered compounds in those subfractions.

IR indicated intramolecular π -bonding of the OH group in approximately one-half of the hydroxyl compounds present in subfraction 2 from the strong acid concentrate. As shown in figure 14, a second OH band at 3550 cm^{-1} was observed in the spectrum of subfraction 2, in addition to the commonly occurring OH band which typically exhibits maximum absorbance anywhere from 3600 to 3580 cm^{-1} . Whenever doublet OH bands have been noted in spectra of petroleum-derived ArOH, the lower wavenumber band has been ascribed to 2-hydroxybiphenyls or similar compounds where the OH group is capable of π -bonding with an aromatic moiety (2,8). Since GC/MS results indicated 2-hydroxybiphenyl homologs in fractions not exhibiting the 3550 cm^{-1} band and since no hydroxybiphenyls or other members of the -14(0) Z-series were detected in subfraction 2 (table 15A), this band must represent some other structure(s) in this case. However, the phenomenon of intramolecular

FIGURE 11. - Mass spectrum of sterically hindered -8(0) (C₁₅H₂₂O) ArOH derivative in subfraction 3 from the SRC-II >325°C weak acid concentrate.

FIGURE 12. - Mass spectrum of a sterically hindered -14(0) (C₁₁-H₂₀O) ArOH derivative in subtraction 4A from the SRC-II >325°C weak acid concentrate.

FIGURE 13. - Mass spectrum of a sterically hindered -16(0) ($C_{16}H_{16}O$) ArOH derivative in subfraction 4A from the SRC-II >325°C weak acid concentrate.

FIGURE 14. - IR spectra of SRC-II >325°C strong acid subfractions. Concentrations (mg/mL CH₂Cl₂) of solutions of 2-4 were 5.5, 10.8 and 9.5, respectively. Note the OH band corresponding to intramolecular π -bonded ArOH in the fraction 2 spectrum, prominent carbonyl bands in the spectrum of subfraction 3, and intense bands corresponding to intermolecular H-bonded OH/NH groups in spectra for subfractions 3 and 4.

π -bonding may explain the relatively rapid elution of this (these) type(s) compared to other ArOH in the later eluting strong acid subfractions. Although intramolecular bonding may be most appropriately termed an "inductive" effect, usually quite rigid steric requirements must be met before it can occur.

Other notable features of IR spectra in figure 14 are the prominent carbonyl bands for subfraction 3 and broad bands representing intermolecular hydrogen-bonded (H-bonded) OH and/or NH groups in subfractions 3 and 4. The general increase in the intensity of the broad band corresponding to H-bonded groups with increasing subfraction number and in strong versus weak acids is consistent with the corresponding trends of greater acidity and decreased steric hindrance discussed above. Also, the poorer overall accounting of subfraction composition from IR measurements on strong acid subfractions, noted in table 13, parallels their increased H-bonding tendency. H-bonded groups are effectively excluded from IR analysis because only bands corresponding to free OH and NH are measured. H-bonding effects were so severe in the case of strong acid subfraction 5 (Ar(OH)₂ compounds) that incomplete dissolution in dichloromethane was obtained. In addition, the resulting spectrum reflected almost entirely H-bonded species.

Carryover of low levels of aromatic hydrocarbons into acid and base fractions from NIE separations has been noted previously (2). In fact, an early NIE procedure incorporated solvent recycling and exhaustive elution of ion exchange resins in order to reduce this effect (143). A novel finding from this work was that carryover of aromatic hydrocarbons into the weak acid fraction resulted from their behavior as acidic compounds, rather than "sloppy chromatography" or other nonideal effects. Virtually all the identified hydrocarbons (table 14A) were based on fluorene-type structures. As illustrated in table 16, these compounds all possess benzylic hydrogens capable of acidic behavior. Fluorene itself titrates as a weak acid in the current NAT procedure (Appendix 3), and reacts with two equivalents of methyl iodide in the NMR derivatization method (Appendix 2). Thus, the rather unique set of hydrocarbons observed in subfraction 1 from the weak acids must reflect a common ability to interact with the anion resin used in the NIE separation. The proportion of hydrocarbons incapable of acidic behavior

(e.g., -18H compounds) was extremely low. Identification of species noted in table 14A was based on GC retention indices, reference mass spectra, and synchronized scanning fluorescence spectra. The latter technique was especially useful for excluding the presence of more common species (e.g., pyrene and chrysene or other benzanthracene/phenanthrene homologs) which typically constitute much higher percentages of coal liquids.

Another surprising result was the apparent greater acidity of benz[g]indole and benz[e]indole compared to carbazole. As noted in table 16, both benzindoles eluted later than carbazole, and an unidentified dibenzindole isomer eluted after all three benzocarbazoles. The presence of benzindoles and other uncommon pyrrolic isomers in petroleum has not been confirmed, or perhaps even investigated. However, given the significantly different separation behavior of those in SRC-II, compared to conventional carbazole-based forms, it is possible that prior results from this and other laboratories which were interpreted as indicating poor separations in fact denoted variable partitioning of distinctly different isomeric forms of pyrrolic compounds.

The natural tendency to regard compounds of the same nominal type and Z-series as identical should generally be avoided during inspection of tables 14 and 15. In some cases, structural differences within a given Z-series eluting over multiple subfractions were addressed in the tables; however, more often than not, analytical limitations prevented such an assessment. Even where precise identifications could not be made, distributions of Z-series over subfractions frequently implied structural differences. For example, detection of -20(0), -22(0), and -24(0) compounds in strong acid subfractions 2 and 4, but not subfraction 3, strongly suggests the presence of significantly different structural forms in subfraction 2 versus subfraction 4.

A striking example of structural effects on separation behavior was revealed during analysis of subfractions from the more recent separation of SRC-II strong acids depicted in figure 9. GC/MS analysis of subfraction 4 revealed two distinct groups of dihydroxybiphenyl components at each nominal

mass, as shown in figure 15. Analysis of subfraction 3 revealed that elution of 2,X'-dihydroxybiphenyls extended forward of the subfraction 3/4 cutpoint, approximately to the point indicated in figure 9. Dihydroxybiphenyls were also the major type present in subfraction 5; however, their spectra suggested that both hydroxyl groups were substituted onto the same aromatic ring in most cases. The sequential HPLC elution of 2,X'-dihydroxybiphenyls, followed by 4,X'- and finally X,X-isomers reflects geometric constraints limiting the degree to which both hydroxyl groups can simultaneously interact with the TMAH-silica. For example, pure compound studies (102) showed very strong retention for 2,3-dihydroxynaphthalene, because the ortho orientation of hydroxyl groups maximized their simultaneous interaction with TMAH-silica. Retention of 1,3- and 1,7-dihydroxynaphthalene was significantly less than for the 2,3-isomer. Resorcinol (1,3-dihydroxybenzene) was retained more than hydroquinone (1,4-dihydroxybenzene), probably because of the tendency of the latter to assume a perpendicular orientation to the silica surface, which maximized the interaction of one hydroxyl group at the expense of the other. Given the free rotation about the bond bridging the two phenyl rings, the stronger retention observed for dihydroxybiphenyls where both hydroxyl groups are on the same ring (X,X-) compared to one OH per ring (X,X'-) is understandable. The generally earlier elution of 2,X'- compared to 4,X'- isomers probably results from steric effects. However, retention of unsubstituted 2,2'-dihydroxybiphenyl was comparable to that of 1,3- or 1,7-dihydroxynaphthalene (102), because its structure provides a particularly favorable orientation of hydroxyl groups for simultaneous interaction with the column packing. Without the insight provided by the GC/MS technique, the occurrence of -14(O₂) species over such a wide range of elution might have been misinterpreted as indicative of peak tailing or some other problem, rather than as a natural consequence of varying orientation of hydroxyl groups.

FIGURE 15. - GC/MS chromatograms of total ion current (A) and selected ion current at m/z 392 (B), of (acylated) subfraction 4 obtained from recent subfractionation of SRC-II >325°C strong acids depicted in figure 9. The two distinct groups of peaks, representing 2,X'- and 4,X'-dihydroxybiphenyl homologs, illustrated in B were observed in all selected ion chromatograms.

As a crosscheck on the recovery of individual components over the subfractions from the weak acid concentrate, the results from GC/MS analysis of subfractions 1-4A were summed (table 14E) and compared with those from direct analysis of the whole concentrate (table 14F). Raw results from analysis of the whole concentrate were significantly higher than obtained from summation of the subfractions because none of the minor species present were detected in the analysis of the whole concentrate. Subsequent correction of the whole concentrate data for total ArOH detected in subfractions 3 and 4A brought the two data sets into much closer agreement. However, the correction factor employed above is conservative because it does not include contributions from minor pyrrolic types not detected, ArOH in subfractions 1 and 2 detected by IR, or any of the components present in subfractions 4B or 5. Analysis of the whole concentrate was also inherently less precise because of the greater number of GC/MS peaks containing multiple components. Considering the above and the typical uncertainty in GC/MS analyses ($\geq \pm 5\%$), the agreement obtained from summation of the subfractions versus the corrected data from direct analysis was well within experimental error. Therefore, no significant losses over the subfractionation were observed in the case of weak acids. The previously discussed losses during TMAH extraction from strong acid subfractions, in addition to the virtual impossibility of direct analysis of the whole strong acids concentrate owing to its more complex composition, prevented a similar comparison of recoveries.

The practical benefits of simplifying composition through subfractionation prior to analyses by GC/MS or other techniques cannot be overstated. As an illustration, figure 16 shows TIC and selected ion current (SIC) chromatograms of (acylated) subfraction 3. The only components in this subfraction detected from analysis of the whole weak acids (figure 10) were benzo[c]carbazole (largest peak in the TIC chromatogram) and 3 or 4 of the smaller peaks representing minor pyrrolic species. The various Z-series of ArOH present were not detected until after subfractionation because their tremendous isomeric complexity (see SIC chromatograms) caused them to elute as a broad envelope which was totally obscured by the dominant pyrrolic benzolog peaks. The presence of relatively saturated ArOH types in SRC or other coal liquids has not been previously reported--in all probability because of interference from coeluting pyrrolic benzologs in fractions obtained on alumina or silica using classical LC methodology.

FIGURE 16. - GC/MS total ion current (TIC) and selected ion current (SIC) chromatograms of (acylated) subfraction 3 from SRC-II >325°C weak acids. Note the isomeric complexity of ArOH trifluoroacetate homologs depicted by SIC plots corresponding to molecular ions for each of the four Z-series.

Also, the importance of the combined acylation-GC/MS approach described in Appendix 4 in the evaluation of the SRC-II subfractions should be emphasized. For example, preliminary identification of even-mass compounds as ArOH was largely based on their tendency to undergo acylation. The relative proportion of components converted to trifluoroacetyl derivatives may be qualitatively determined by inspection of TIC chromatograms obtained before and after reaction or by comparison of m/z 69 (CF_3+) SIC versus TIC chromatograms. For example, figure 17 shows the typical increase in volatility of ArOH after acylation. The m/z 69 SIC chromatogram (not shown) of the acylated subfraction indicated that the great majority of the components in the subfraction, except benzo[c]carbazole, reacted. GC/MS analysis of $Ar(OH)_2$, such as the dihydroxybiphenyls discussed above, is virtually impossible without prior derivatization because of their low volatility and high polarity. Also, the increase in mass resulting from addition of the trifluoroacetyl group(s), in conjunction with their enhanced volatility, enables detection of derivatized ArOH via molecular ion-SIC chromatograms (e.g., figure 16) in the presence of significant levels of interferences. Additional advantages of the approach are discussed in Appendix 4.

Two important questions which were unresolved in this work were: 1) the identity of the carbonyl type(s) indicated by IR (table 13), and 2) the failure to account for the significant elemental nitrogen content of the strong acid concentrate (0.98%, table 12). Possible explanations for the lack of GC/MS detection of carbonyl compounds include: 1) poor peak shape or nonelution from the GC column, 2) extensive fragmentation and/or lack of significant molecular ions in their mass spectra, or 3) reaction with trifluoroacetyl chloride (e.g., through enol or other tautomeric forms) and misidentification as ArOH. Explanations for the missing nitrogen compounds in strong acid subfractions include the first two cited for carbonyls, and 3) loss during TMAH extraction. Solution of the nitrogen problem was hampered by the insufficient quantities of subfractions for elemental N analysis. An attempt was made to screen selected fractions for nitrogen-containing compounds using GC with FID and N/S selective detectors as described in the Experimental section. Figure 18 shows a typical result for an acylated fraction; the only nitrogen-containing compounds detected corresponded to minor peaks in the FID trace. The acylation procedure in use at the time was

FIGURE 17. - GC/MS total ion current (TIC) chromatograms of subfraction 4A from SRC-II >325°C weak acids before (A) and after (B) acylation. Note the increased volatility (see dotted line) of the large hump representing ArOH trifluoroacetate esters in (B).

FIGURE 18. - GC analysis of (acylated) SRC-II >325°C strong acid subfraction 5 with three-way detection. The relative detector responses show that none of the major components eluted contains either sulfur or nitrogen.

incapable of derivatizing most acidic N-H groups and many $\text{Ar}(\text{OH})_2$ species. Had the current procedure been available, more nitrogen-containing species might have been detected. Underivatized fractions exhibited few, if any, nitrogen-containing peaks (103).

A potentially related problem was the poor IR accounting of compound types in selected subfractions (table 13). IR results for compound types in weak acid subfractions 1-4A agreed well with totals from GC/MS analysis (tables 14A-D) and totaled near 100% (recall that subfraction 1 contained 80+% hydrocarbons). IR totals for all other subfractions were well below 100%. As explained earlier, one plausible explanation for the low results was that H-bonding lowered the intensity of free OH, and potentially NH, bands. However, recent rechecking of those results using the method in Appendix 1 yielded OH contents in good agreement with those determined originally (see data in parentheses shown in the table). Thus, the H-bonded region in the original spectra (figure 14) may depict N-H groups, entrapped water, or another functional group and/or phenomenon. An alternate explanation of the low IR results was use of incorrect MW in the calculation of IR data. However, independent checks of the MW determined by GC/MS (tables 14 and 15) by NAT (Appendix 3) yielded only slightly higher results for average MW; e.g., 258 (NAT) versus 215 (GC/MS) for subfraction 4. The higher NAT MW result is consistent with incomplete elution of higher MW ArOH from the GC, resulting in a low GC/MS estimate for average MW.

Although resolution of the remaining ambiguities in the SRC-II analysis may be useful toward further defining separation behavior, the available results still constitute a significant description of separation selectivity achievable with the HPLC and NIE procedures. These results also provided useful guidelines for further development of the HPLC method and application to petroleum. Listed below are the major conclusions from the work.

- The elution order of acidic classes and compounds within a given class is a function of their relative acidity and steric factors affecting their ability to interact with the anion exchange resin, in the case of the NIE separation, and TMAH-silica in the case of the HPLC subfractionation method.

- The observed behavior of SRC-II compounds correlated well with that predicted from pure compound studies. However, the overlap between compound classes was greater than indicated by simple mixtures of pure components

because of the much greater structural variety of components in the SRC-II acid concentrates.

- NIE preseparation of acids into strong and weak types significantly reduced overlap of compound classes in the subsequent HPLC subfractionation step.
- HPLC subfractionation facilitates detailed analysis of acid concentrates by reducing the overall sample complexity and number of classes present in a given fraction to a level more consistent with the resolution capabilities of available instrumentation.
- Aromatic hydrocarbons present in the weak acid concentrate contained benzylic hydrogens capable of acidic behavior.
- The only significant practical problem encountered was sample loss during TMAH extraction. The aqueous extraction procedure for TMAH removal was clearly the weak link in the overall separation sequence.
- The level of information attainable from analysis of acid subfractions is currently limited by the availability of reference spectral and chromatographic data.

Separation and Analysis of Wilmington 370-535° C Acids

As discussed in Chapter 2 and elsewhere (144), the performance of batches of ion exchange resin prepared for NIE separations is routinely monitored by yields of acids or bases obtained from separation of a Wilmington, CA, 370-535° C distillate. Yields of total acids from acceptable batches of anion exchange resins range from 9.7 to 10.7 wt % of the distillate.

A number of these acid concentrates were composited and subfractionated using current conditions specified in table 8. Figure 19 shows representative HPLC chromatograms. TMAH was removed from the resulting subfractions by adsorption onto BioRex 70 ion exchange resin as described in the Experimental section. Through repetitive separations, a sufficient quantity of the composited acid concentrate was fractionated (3 g) to provide adequate amounts of most subfractions for elemental, NMR, IR, and NAT analysis using current versions of the latter three techniques described in the appendices. The objective of the work was to assess the capabilities of present versions of the separation and analytical techniques for determination of compound classes in petroleum.

FIGURE 19. - HPLC chromatograms of the current standard blend (A) (see table 9) and Wilmington 370-535°C composite total acid concentrate (B) obtained using conditions specified in table 8. See table 17 for subfraction yields and elemental content.

Table 17 shows yields and elemental content of the subfractions. The excellent mass recovery and agreement between elemental balances calculated over the subfractions versus results for the whole acid concentrate demonstrate that both quantitative recovery and TMAH removal were achieved. The slight discrepancy in results for elemental carbon may reflect the presence of a small amount (~0.5 wt %) of water or formic acid in the composited acid concentrate. The higher nitrogen content of lower number subfractions and opposite trend for oxygen reflect the anticipated elution order of major classes: pyrrolic benzologs, ArOH, and carboxylic acids, respectively. Results for sulfur approximately paralleled those for oxygen, except that the significant increase in oxygen content from subfraction 4 to 5 was not reflected in the sulfur data, which actually decreased slightly.

TABLE 17. - Mass and elemental balances obtained from HPLC subfractionation of Wilmington 370-535° C total acids

Subfrac- tion No. ¹	Yield, Wt. % Total Acids	Elemental Content, Wt % Subfraction					O ³
		C	H	H/C ²	N	S	
1	16.2	84.84	9.46	1.329	2.78	0.48	2.44
2A	18.8	85.32	9.26	1.293	3.20	0.27	1.95
2B	29.3	84.76	8.93	1.255	3.23	0.55	2.53
3	9.5	79.96	8.94	1.332	1.71	1.68	7.71
4	25.6	77.84	10.66	1.633	0.42	1.61	9.47
5	0.5	69.24	8.30	1.428	0.85	1.36	20.25
Balance ⁴	99.9	82.49	9.51	1.378	2.27	0.87	4.76
Whole ⁵	--	81.92	9.46	1.376	2.27	0.91	5.44

¹See figure 19.

²Atomic ratio

³By difference

⁴Calculated from subfraction data

⁵Determined from analysis of total acids

Table 18 summarizes NAT results. All fractions exhibited multiple endpoints (EP); the equivalent weight (EQ WT) was calculated from the sum of all endpoints (EP_T) observed (EQ WT = 1000/EP_T). EQ WT results were used as

estimates of average molecular weight in calculations of subsequent IR and NMR results. The balance data calculated from NAT results for the subfractions were in reasonable agreement with those determined directly from titration of the total acids. Except for simple mixtures, e.g., 2-4 components, rigorous balances of NAT results are not generally obtained (e.g., as with elemental data) because the distribution of compounds present in a given fraction, especially those titrating near a given EP, affects its precise location (104).

TABLE 18. Nonaqueous titration (NAT) results for Wilmington 370-535° C total acids and subfractions

A. Raw Data

Subfrac- tion No.	EP (meq/g)				HNP (mv)			EQ WT (mg/meq)
	1	2	3	Total	1	2	3	
1	0.37	2.01	-	2.37	-120	-500	-	420
2A	0.27	2.52	-	2.79	-145	-470	-	358
2B	0.20	2.68	-	2.88	-70	-485	-	347
3	0.66	1.41	0.49	2.56	-120	-410	-640	391
4	2.57	0.13	-	2.70	-150	-590	-	370
5	2.86	0.42	-	3.28	-130	-590	-	305
Balance ¹	0.90	1.71	0.09	2.70	-140	-480	-620	370
Whole ²	1.02	1.54	0.29	2.85	-135	-460	-640	351

B. Relative Distribution of Acidic Types (%)

Subfraction No.	Strong ³	Weak ⁴	Very Weak ⁵
1	16	84	-
2A	10	90	-
2B	7	93	-
3	26	55	19
4	95	5	-
5	87	13	-
Balance ¹	33	63	4
Whole ²	36	54	10

¹ Calculated from subfraction data

² Determined directly from titration of total acids

³ HNP = (-70) - (-150) mv

⁴ HNP = (-400) - (-500) mv

⁵ HNP = (-590) - (-640) mv

As discussed in Appendix 3, the half neutralization potential (HNP) of a given EP reflects the average acidity of the species titrated in an analogous manner to pK_a measured in aqueous media. Acidity increases as HNP approaches zero; very strong acids such as sulfonic acids exhibit positive HNP's. Thus, the results in the table indicate significantly higher proportions of relatively strong (HNP ca.-140 mv) acids in later eluting subfractions, as expected. It should be noted that the apparent acidity of selected classes in dimethyl sulfoxide (DMSO, the solvent used in the NAT procedure) differs significantly from that in aqueous systems (see Appendix 3 and ref. 100). For example, both the monoketone anthrone and several diones exhibit acidities equivalent to that of carboxylic acids in DMSO, while behaving as very weak acids in water. Also, the acidity of thiophenol is significantly greater than that of benzoic acid in DMSO, while the reverse holds true for their behavior in water. For this reason, and because the HNP's of many classes overlap, EP's exhibiting similar HNP's should not be assumed to reflect relative proportions of the same class in two different fractions without supporting information from other techniques.

Table 19 shows IR results. Molar absorptivities (ϵ) used in the calculation of each compound type are indicated in footnotes in the table. The basis for ϵ 's used in the calculation of OH (direct), OH (after acylation) and carboxyl content is discussed in Appendix 1. The difference in absolute magnitude of ϵ 's given in the appendix versus those used here is largely attributable to an overhaul of the IR instrument performed in the interim, which changed its response characteristics somewhat. The dependence of ϵ on instrument and cell characteristics is discussed in Appendix 1; independent calibration and periodic rechecking of response factors for each functional group measured are essential for obtaining reliable quantitative data. The ϵ of benzo[a]carbazole ($174 \text{ L mol}^{-1} \text{ cm}^{-1}$) was used in calculation of NH types because of its previously cited abundance in acid fractions from this and analogous distillates from other petroleum (2). By default, the ϵ for carboxyl-type carbonyls was also employed in the calculation of unidentified carbonyl types absorbing in the regions $1710\text{--}1700$ and $1660\text{--}1650 \text{ cm}^{-1}$. By far, the necessity of assuming representative response factors (ϵ) is the major limitation in accuracy attainable from quantitative IR applied to petroleum or analogous complex mixtures.

TABLE 19. Infrared results for Wilmington 370-535° C total acids and subfractions¹

Subfrac- tion No.	Compound Type, Wt. %						Total ⁵
	OH ²		NH ³	RCOOH ⁴	Other C=O ⁴		
	Direct	Acylated		1700-1710 cm ⁻¹	1650-1660 cm ⁻¹		
1	7	15	44	-	14	9	82
2A	10	16	65	-	8	11	100
2B	21	18	68	-	8	12	106
3	35	50	22	9	11	10	102
4	5	11	nd ⁶	90	-	-	101
5	nd	ND ⁷	nd	44	-	-	44
Balance	14	18	41	24	7	8 ⁸	98
Total	17	16	47	37 ⁹	-	-	101

¹EQ WT in Table 18 were used as average molecular weights in all calculations

² ϵ 's assumed in calculations were 143 (direct) and 606 (acylated) l. mol⁻¹ cm⁻¹

³ ϵ assumed in calculation was 174 l. mol⁻¹ cm⁻¹

⁴ ϵ 's assumed in calculation of all C=O types was 710 l. mol⁻¹ cm⁻¹

⁵Total reflects OH result determined via acylation

⁶None detected

⁷Not determined

⁸Total C=O types is 24+7+8 = 39 wt. %

⁹"RCOOH" determined from total acids is effectively total carbonyl types

Total OH results determined from IR measurement of acylated fractions typically exceeded those from direct (without acylation) measurement by up to a factor of two. As discussed in conjunction with SRC-II IR data, and in Appendix 1, direct OH determinations are frequently too low because hydrogen-bonding decreases the intensity of the IR band corresponding to free OH groups.

Using the OH data obtained via acylation, the sums of the functional groups determined by IR total reasonably close to 100%, except in the case of subfraction 5. The small size and high polarity of the latter made it difficult to quantitate by IR. However, in spite of problems with subfraction 5, acceptable agreement was obtained between balance data calculated from the subfractions versus those determined on the whole acid concentrate.

As with the SRC-II weak acids, extensive overlap of OH and NH types was indicated from the IR analysis of Wilmington subfractions. Furthermore, both types constituted significant proportions of subfraction 1 from the Wilmington acids, whereas their elution did not start until subfraction 2 in the case of SRC-II. The only Wilmington subfractions containing predominantly one type were 4 and 5, which largely contained carboxylic acids. Because of its

greater structural diversity and higher degree of alkylation, the Wilmington acid-concentrate was a much more severe test of the HPLC method than the SRC-II acids. Thus, as confirmed by the NMR results given below, structural effects on separation behavior revealed in analysis of SRC-II subfractions were greatly magnified in the case of Wilmington.

Table 20 summarizes results from NMR analysis of $^{13}\text{CH}_3\text{I}/^{12}\text{CH}_3\text{I}$ -methylation products of subfractions and total acids discussed in detail in Appendix 2. Data in the appendix were modified slightly to reflect the current NAT equivalent weights in table 18; the corrected results are given in table 20. The NMR data generally confirm IR results for types determined by both techniques. However, the NMR method is more sensitive and, in all probability, more accurate than IR. The only potential limitations on accuracy attainable by the NMR approach are from spectral overlap or incomplete methylation of selected acidic classes or types.

TABLE 20. NMR results for Wilmington 370-535° C total acids and subfractions¹

A. Average Number of Functional Groups Per Molecule

Subfrac- tion No.	Benzylic H/SH	NH	COOH	OH	OH (Hindered)	Total
1	0.06	0.67	0.07	0.02	0.12	0.94
2A	0.02	0.85	0.06	0.02	0.12	1.07
2B	0.05	0.79	0.05	0.18	0.12	1.19
3	0.09	0.37	0.19	0.64	0.17	1.46
4	0.08	0.12	1.00	0.03	0.04	1.27
Balance ²	0.06	0.56	0.31	0.13	0.10	1.16
Total	0.09	0.68	0.39	0.14	0.14	1.44

B. Relative Percentage of Each Functional Group

1	6	71	7	2	13	99
2A	2	79	6	2	11	100
2B	4	66	4	15	10	99
3	6	25	13	44	12	100
4	6	9	79	2	3	99
Balance ²	5	48	27	11	9	100
Total	6	47	27	10	10	100

¹EQ WT data in Table 18 were used as average molecular weights in all calculations

²Subfraction 5 (0.5 wt % total acids) was not analyzed by NMR. Balance reflects results for subfractions 1-4.

The NMR results show an even greater degree of compound class overlap than apparent from IR analysis. To an approximation, detectable levels of all functional groups were found in every subfraction, although their proportions (table 20B) varied significantly. Also, except for subfraction 1, the results show that a significant proportion of Wilmington acids contain more than one functional group.

In order to better correlate elemental composition with functional group content, the raw elemental data in table 17 were converted to a form analogous to that used in table 20A for expressing NMR functional group results. Table 21 shows the results of these calculations, which also assume EQ WT data expressed in table 18 as the respective average molecular weights for each fraction. Because of the prevalence of O_2 -types (carboxylic acids), elemental oxygen content was further divided between single O and O_2 -types according to the OH/COOH ratio indicated by NMR (table 20). Even after accounting for the presence of O_2 -types, the elemental data generally show greater numbers of heteroatoms per molecule than indicated by NMR functional group analysis. These "extra" heteroatoms are presumably present in nonacidic functional groups or in unaccounted for multiple-heteroatom groups such as the amide functionality.

TABLE 21. Heteroatom distributions in Wilmington 370-535° C total acids and subfractions calculated from elemental composition and NMR¹

Subfrac- tion No.	Average number of heteroatoms per molecule					Total ²
	N	S	Total	O	O ₂	
1	0.834	0.063	0.64	0.32	0.16	1.38
2A	0.817	0.030	0.44	0.24	0.10	1.19
2B	0.801	0.060	0.55	0.41	0.07	1.34
3	0.478	0.205	1.88	1.28	0.30	2.26
4	0.112	0.186	2.19	0.07	1.06	1.44
5	0.185	0.129	3.86	-	1.93	2.24
Balance	0.600	0.100	1.10	0.30	0.40	1.40
Total	0.569	0.100	1.19	0.31	0.44	1.42

¹From elemental data in Table 17. The ratio of OH/COOH types determined by NMR (Table 20) was used to factor total elemental oxygen content into O vs O_2 types. EQ WT data in Table 18 were used as average molecular weight in all calculations.

²Total = N + S + O + O_2

Correlation of all available data resulted in the summary of subfraction and total acid composition provided in table 22A. The primary basis for determining composition was elemental content (table 21); NMR data (table 20A) were then used to compute functional group distributions for the bulk of each heteroatom present; the proportions unaccounted for by NMR were either assigned to nonacidic forms or to some other type based on IR and/or NAT results (tables 18 and 19). The relative distribution of a given functional group over the subfractions (table 22B) was computed from results in table 22A and the gravimetric yields of subfractions listed earlier in table 17.

The results in table 22A dramatically illustrate the complexity of the Wilmington acid fraction. The number of functional groups, some of which by definition contain two heteroatoms (carboxyl and amide), ranged from slightly over one to over two per average molecule. The majority of compounds present in subfractions 1, 2A, and 2B were monofunctional, whereas the later eluting subfractions contained mostly difunctional and/or carboxylic types.

The wide range of elution (table 22B) for each class is an effective measure of structural diversity within each class. In selected cases, such as resolution of hindered versus nonhindered OH types by NMR, some indication of structural differences accounting for variability in separation behavior was provided. In most, however, separation behavior was the only available indicator for structural variability.

The apparent elution of compounds containing relatively acidic groups--e.g, carboxyls--into subfraction 1 (unretained components) was particularly surprising. Figure 20 compares the carbonyl region of IR spectra of subfraction 1 versus 4. Subfraction 4 shows carbonyl bands characteristic of carboxyl groups (bands corresponding to monomeric species at 1750 cm^{-1} and H-bonded dimers at 1710 cm^{-1}) while subfraction 1 exhibits a single band at 1705 cm^{-1} (in addition to a band tentatively assigned to amide groups at 1655 cm^{-1}). If the 1705 cm^{-1} band in the subfraction 1 spectrum does indeed represent carboxyl groups, as indicated by correlations with NAT and NMR data, they clearly exist in a different chemical environment than those in subfraction 4. The absence of a band corresponding to "free" carboxyl groups (ca. 1750 cm^{-1}), suggests that carboxyl groups in subfraction 1 are intramolecularly-bonded to another group or moiety. For example, IR spectra indicated π -bonding of selected types of OH groups in early eluting SRC-II subfractions. In any case, the above, or an analogous effect, must greatly

Table 22. - Summary of compound classes present in Wilmington 370-535° C total acids and subfractions ¹

A. Average Number of Functional Groups Per Molecule

Subfraction No.	Sulfur Containing			Nitrogen Containing				Oxygen Containing						TOTAL
	Thiol	Sulfide, Thiophenic, or Other	Total	Pyrrolic	Amide	Pyridinic or other non-NH Types	Total	ArOH	ArOH (Hindered)	COOH	Amide	Ether or Other non-acidic Types	Total	
1	0.06	nd ²	0.06	0.58	0.09	0.16	0.83	0.02	0.12	0.14	0.09	0.04	0.41	1.21
2A	0.02	0.01	0.03	0.71	0.11	nd	0.82	0.02	0.12	0.08	0.11	nd	0.33	1.07
2B	0.05	0.01	0.06	0.68	0.12	0.01	0.80	0.18	0.12	0.06	0.12	nd	0.48	1.22
3	0.09	0.12	0.21	0.27	0.10	0.11	0.48	0.64	0.17	0.21	0.10	0.44	1.56	2.15
4	0.08	0.11	0.19	≤0.12	ND	nd	0.11	0.03	0.04	1.00	ND	<0.06	1.13	1.43
5	ND ³	ND	0.13	ND	ND	ND	0.19	ND	ND	~1.93	ND	~0	1.93	2.25
Balance	≥0.06	≤0.04	0.10	≤0.48	≥0.08	0.04	0.60	≥0.13	≥0.10	0.34	≥0.08	≤0.06	0.72	1.33
Total	0.09	0.01	0.10	0.47	ND	ND	0.57	0.14	0.14	0.39	ND	<0.08	0.75	<1.42

B. Normalized Distribution of Functional Groups over the Subfractions

	TOTAL MASS													TOTAL MASS
	1	2A	2B	3	4	5	Balance	1	2A	2B	3	4	5	
1	17	6	25	16	36	ND	100	nd	4	7	26	63	1	16.2
2A	6	25	16	36	ND	100	100	4	7	26	63	1	100	18.8
2B	25	16	36	ND	100	100	100	7	26	63	1	100	100	29.3
3	16	36	ND	100	100	100	100	26	63	1	100	100	100	9.5
4	36	ND	100	100	100	100	100	63	1	100	100	100	100	25.6
5	ND	100	100	100	100	100	100	1	100	100	100	100	100	0.5
Balance	100	100	100	100	100	100	100	100	100	100	100	100	100	99.9

¹ Combined correlations from Tables 18-21

² None detected

³ Not determined

FIGURE 20. - Portions of IR spectra showing carbonyl bands in subfractions 1 vs. 4 from the Wilmington 370-535°C total acid concentrate. Concentrations (mg/mL CH_2Cl_2) were 11.9 and 6.0, respectively. Note the classical carboxyl monomer/dimer pattern in the spectrum of subfraction 4 vs. the occurrence of a single band at 1705 cm^{-1} , with shoulder peaks at 1706 and 1730 cm^{-1} , in the subfraction 1 spectrum.

diminish the ability of carboxyl groups in subfraction 1 and other early eluting subfractions to interact with the HPLC column packing; otherwise, they would elute along with the bulk of the carboxylic acids into subfraction 4.

Although they did not indicate the degree of compound class separation hoped for, the results from the various functional group methods correlated quite well with one another and with elemental composition. Figures 21-24 show correlations of elemental composition versus functional group content of subfractions, total acids and the total balance calculated from subfraction results. Subscripts included with points in the figures denote subfraction number, total (T) or balance (B). For example, figure 21 shows the excellent agreement in results for total carboxyls obtained by NMR versus total strong acids determined by NAT (table 18B). Also, the carboxyl assignment for IR bands observed near 1710 cm^{-1} in spectra of subfractions 1-3 appears justified in light of their correlation with the other values for carboxyl content.

The greater scatter in results for single oxygen compounds shown in figure 22 and their poorer agreement with elemental composition result from the presence of oxygen in nonacidic (e.g., ether) groups and the differences in parameters determined by IR versus NMR. Thus, while the IR correlation includes oxygen present in both OH and amide groups, the NMR technique is capable of detecting OH groups exhibiting a higher degree of steric hindrance. For example, highly hindered 2,6-di-tert-butylphenol homologs undergo methylation and are detected by the NMR method but are inert toward acylation and thus would be excluded from IR results.

Figure 23 shows good correlation between elemental nitrogen versus total NH types measured by IR or NMR except in the case of subfraction 1. As noted in table 22A, subfraction 1 apparently contains a moderate level of tertiary nitrogen in pyridinic-type or analogous structures. These compounds either also contain an acidic group or represent basic contaminants. In either case, they comprise only about 13% of subfraction 1 or 2% of the total acid fraction. The assignment of the IR carbonyl band occurring near 1650 cm^{-1} to amide groups is based on the resulting improvement provided in correlations of IR versus NMR data in figures 22 and 23, as well as analogous assignments made in the literature (2,7-10,55).

FIGURE 21. - Correlation of the average number of carboxyl (O₂) groups per molecule indicated by elemental content vs. NMR, IR or NAT techniques.

FIGURE 22. - Correlation of the average number of single oxygen functional groups per molecule indicated by elemental content vs. levels of specific functional groups detected by NMR or IR.

FIGURE 23. - Correlation of the average number of nitrogen atoms vs. NH functional groups per molecule.

FIGURE 24. - Correlation of the average number of sulfur atoms vs. NMR-determined SH/benzylic H groups per molecule.

The direct correlation between elemental sulfur content versus NMR results for benzylic and/or thiol groups for early eluting subfractions (1, 2A, and 2B) in figure 24 suggests the presence of low levels of thiols in those subfractions. The much higher elemental sulfur content of later eluting subfractions, relative to NMR results, indicates that other sulfur forms predominate in those fractions. Perhaps of even greater interest is the apparent lack of benzylic structures (e.g., fluorene) in the Wilmington acids. The reader will recall that over 80% of subfraction 1 from the SRC-II weak acid concentrate consisted of aromatic hydrocarbons with benzylic hydrogens.

The above analysis of the Wilmington acids demonstrated two key points: 1) that development of analytical methods had progressed to the point where subfractionation was no longer necessary to simply determine functional groups present in a given acid concentrate, and 2) the only justification for performing subfractionations was for detailed analysis of structural variability within the major classes present. The first point is demonstrated by the general agreement between balances calculated from analysis of individual subfractions versus results obtained directly on the total acid concentrate (tables 17-22). Although on one hand it may be argued that the agreement obtained demonstrates viability of the subfractionation procedure, it also shows that direct analysis yields equivalent results without the expense and labor of additional separations. The second point may also be approached from different perspectives. From one viewpoint, it may have been preferable to have clearly separated each class into different fractions. On the other hand, structural differences within each class would then have to be assessed purely by instrumental means or through additional separations. From the latter perspective, given the capability to determine compound classes with the available methods, the observed separation behavior is preferred, since it clearly reflects structural differences within each class.

Two significant questions were also raised by the findings: 1) are the apparent structural effects on separation behavior unique to the TMAH-silica system, and 2) is the observed distribution of compound classes strictly

derived from structural effects or did other factors (human error, instrumental malfunctions, column overload, etc.) contribute? These questions may be addressed by examination of separation data and composition of subfractions obtained from earlier separations of comparable Wilmington acid concentrates using initial HPLC conditions (137).

Figure 25 shows a representative HPLC chromatogram from subfractionation of a comparable Wilmington 370-535° C total acid concentrate obtained with initial HPLC conditions specified in table 6 ("B"-cutpoints). A chromatogram of the standard (table 7) is included for convenient reference. The differences in separations of Wilmington acids apparent from comparison of figures 25 versus 19 are similar to those noted earlier for SRC-II acids separated under initial versus current conditions (see discussion of figures 7-9). Although the composition of subfractions obtained from figures 25 versus 19 could be rigorously compared on the basis of a detailed correlation of gradient programs, column efficiencies, retention of standard components, fraction cutpoints relative to standard components, etc.; relative subfraction yields provide a much simpler means for comparing the two separations. Figure 26 shows mass balances from the separations in figures 19 versus 25, as well as those from independent separations of strong and weak acid concentrates. Initial HPLC conditions were also used for separation of the strong and weak acid concentration.

Figure 27 shows representative chromatograms obtained from subfractionation of the strong and weak acid concentrates (4.97 and 5.15 wt % of the total distillate, respectively). The qualitative differences in chromatograms for weak versus strong Wilmington acid concentrates are not as great as those noted earlier for the corresponding SRC-II concentrates (figure 7). For Wilmington, the only obvious distinction is the prominent peak corresponding to carboxylic acids in the strong acid concentrate which is effectively absent in the weak acid chromatogram.

FIGURE 25. - HPLC chromatograms of the standard blend (table 7) and Wilmington 370-535°C total acids obtained using initial conditions specified in table 6 ("B"-cutpoints). Compare with figure 19.

FIGURE 26. - Subfractionation yields from separation of Wilmington 370-535°C total acids obtained with current (figure 19) vs. initial (figure 25) experimental conditions compared to yields from subfractionation of individual strong and weak acid concentrates obtained using initial HPLC conditions (figure 27). Data inside boxes denote subfraction yields (wt % total acids); subfraction designations appear at right.

FIGURE 27. - HPLC chromatograms from subfractionation of weak vs. strong Wilmington 370-535°C NIE acid concentrates. Yields of weak and strong acids (wt % distillate) were 5.15 and 4.97, respectively, as compared to 10.06 for the total NIE acids depicted in figure 25. Experimental conditions as specified in table 6 ("B"-cutpoints).

Subsequent comparison of IR spectra of subfractions from the two separations of total acid concentrates (figures 19 vs. 25) showed qualitatively equivalent distributions of compound classes in corresponding subfractions. Because of the inexact correspondence of any given pair of subfractions (see figure 26), a detailed quantitative IR comparison was not made. In addition, crosschecks of elemental composition confirmed the similar distribution of classes obtained over the two separations. Therefore, this independent verification of separation behavior effectively eliminated the possibility of human error, instrument malfunction, or similar problems having had a significant impact on results in tables 17-22.

The mass balances obtained from subfractionation of strong versus weak acids (figure 26) support a similar selectivity over the NIE versus HPLC methods. For example, the bulk of the weak acid concentrate elutes into subfractions 1 and 2, which indicates that compounds with weak retention in the NIE separation are also generally weakly retained in the HPLC system. The same effect was observed during separation of the SRC-II acids discussed earlier. However, a more detailed analysis of subfractions from the strong versus weak acid concentrates was needed in order to determine if structural effects governing partitioning into strong versus weak types could be related to those affecting the HPLC subfractionation. Because of its simplicity and applicability to the relatively small quantities of subfractions available, NAT was the primary technique used in the evaluation.

Tables 23A and 23B show the results obtained on subfractions from strong versus weak acid concentrates, respectively. In addition, those results were used to calculate a set of NAT data corresponding to subfractions from separation of a total acid concentrate (table 23C). Mass balances from subfractionation of strong and weak acid concentrates (figure 26) and their respective yields from the 370-535° C distillate (noted above and in figure 27) were used as weighting factors in the calculation of data for table 23C. Finally, results in tables 23 A-C are expressed on a relative basis in table 23D.

TABLE 23. - Nonaqueous titration (NAT) results for Wilmington 370-535°C
weak and strong acid concentrates and subfractions thereof

Subfraction No.	EP (meq/g)				HNP (mv)			EQ WT mg/meq
	1	2	3	Total	1	2	3	
A. Strong								
1	0.88	0.88	0.87	2.63	-60	-260	-590	380
2	0.90	2.02	-	2.92	-40	-330	-	343
3	0.71 ₂	1.38	1.00	3.09	-15	-270	-565	324
4	ND							
5	2.80	0.05	-	2.85	-75	-530	-	351
6	2.47	0.51	-	2.98	-115	-500	-	336
Balance ³	1.77	0.90	0.22	2.89	-70	-310	-570	346
Total	1.77	0.93	0.28	2.98	-90	-260	-550	336
B. Weak								
1	0.52	1.59	0.36	2.47	-20	-410	-590	405
2	0.40	2.65	-	3.05	-30	-440	-	328
3	1.23	2.82	-	4.05	-105	-585	-	247
4	0.85	2.31	-	3.16	-90	-595	-	317
5	ND							
6	1.97	0.28	-	2.25	-95	-480	-	444
Balance ⁴	0.56	2.07	0.40	3.03	-40	-430	-590	331
Total	0.53	2.47	-	3.00	-70	-470	-	333
C. Combined ⁵								
1	0.58	1.47	0.45	2.50	-30	-390	-590	400
2	0.59	2.41	-	3.00	-40	-400	-	333
3	0.91	0.83	1.73	3.47	-60	-270	-570	288
4	0.76	0.87	1.49	3.12	-40	-270	-580	321
5	2.64	0.24	-	2.88	-75	-580	-	347
6	2.22	0.39	-	2.61	-105	-500	-	383
Balance	1.15	1.49	0.31	2.95	-60	-400	-590	339
Total	1.14	1.71	0.14	2.99	-85	-410	-550	334

¹ See figures 26 and 27.

² Not determined.

³ Results obtained for subfraction 3 were assumed to hold for subfraction 4 in the calculation of balance data.

⁴ Results obtained for subfraction 4 were assumed to hold for subfraction 5 in the calculation of balance data.

⁵ Calculated from results for strong and weak concentrates.

TABLE 23. - Nonaqueous titration (NAT) results for Wilmington 370-535°C
weak and strong acid concentrates and subfractions thereof (cont)

D. Relative distribution of acidic types (%)

Subfraction No.	Concentrate	Strong ⁶	Weak ⁷	Very Weak ⁸
1	Weak	21	64	15
	Strong	33	33	33
	Total	23	59	18
2	Weak	13	87	-
	Strong	31	69	-
	Total	20	80	-
3	Weak	30	-	70
	Strong	23	45	32
	Total	26	24	50
4	Weak	27	-	73
	Strong	ND		
	Total	24	28	48
5	Weak	ND		
	Strong	98	-	2
	Total	92	-	8
6	Weak	88	12	-
	Strong	83	17	-
	Total	85	15	-
Balance	Weak	19	68	13
	Strong	61	31	8
	Total	39	51	10
Total	Weak	18	82	-
	Strong	59	31	10
	Total	38	57	5

⁶ HNP = (-20)-(-120) mv

⁷ HNP = (-250)-(-500) mv

⁸ HNP = (-530)-(-600) mv

Assuming the previously demonstrated (figure 21) 1:1 correlation between carboxylic groups and "strong acids" determined by NAT, the results in table 23 clearly demonstrate significant proportions of carboxylic acids in both the strong and weak acid concentrates. Overall (see balance or total acid data, table 23D), 19 wt % of the weak acid concentrate titrated at an HNP consistent with neutralization of carboxyl groups, as compared to 60 wt % for the strong acid concentrate. Given the nearly equal yields of strong versus weak acid from the whole distillate, the above data correspond to partitioning of about 24% of the total carboxylic acids into the weak acids and 76% into strong acids over the NIE separation. This distribution compares very favorably with that from HPLC separation of total acids (table 22B), where 78% of the carboxylic types eluted into subfractions 4 and 5 (the fractions anticipated to contain carboxylic acids) and the remaining 22% eluted into earlier fractions. However, structural effects on separation behavior of carboxylic acids in the NIE versus HPLC procedures were not identical; for example, some carboxylic acids in the strong acid concentrate exhibited relatively weak retention during HPLC subfractionation.

Further evaluation of the above as well as IR data led to the same general conclusion: structural effects on separation behavior in the NIE versus HPLC methods were related, but not identical. One surprisingly large difference was in the behavior of amides; based on IR spectra, they eluted relatively rapidly in the HPLC separation yet appeared to be retained exclusively as strong acids in the NIE separation. Comparison of data in tables 23C and 18 revealed surprisingly good correspondence between NAT results for subfractions from initial versus current separation conditions; the greatest difference was the higher proportion of strong (HNP (-20)-(-150)) acids in early eluting subfractions obtained with the initial HPLC conditions.

In view of the above, it was concluded that 1) the results summarized earlier in table 22 were representative of those obtainable with the TMAH-silica method, and 2) that the rather extensive overlap of compound classes observed for the subfractionation occurred over NIE separation as well, and thus reflected the structural variability within the Wilmington acids more than any other factor.

Overall, separation and analysis of the Wilmington 370-535° C acids demonstrated the viability of the NAT, IR and NMR techniques and showed good intercorrelation of results from each with elemental composition. The performance of the NMR technique was especially impressive; by itself, it can determine the majority of important classes in a whole acid fraction. The major conclusions concerning the performance of the separations are basically the same as those listed earlier at the end of the section on SRC-II acids. However, points made there concerning class overlap from structural variety were understated in proportion to the effects observed for Wilmington acids. As noted earlier, the main justification for performing subfractionations of complex acid concentrates like Wilmington would be subclassification of each class according to separation characteristics.

Effects of NIE Methodology on Subfraction Distributions

Not surprisingly, the main effect on acid subfraction distributions noted during development of the NIE procedure (Chapter 2) was a steady increase in the proportion of material eluting into subfractions 1 and 2. The increasing yield of subfractions enriched in weaker acids simply reflected the greater efficiency of new batches of ion exchange resins toward their isolation. Table 24 illustrates typical results.

Comparison of results for the Wilmington 370-535° C distillate acids discussed in the preceding section with those of McKay et al. (2) on the identical distillate revealed comparable levels of carboxylic acids, on a whole distillate basis, from the two analyses. However, much higher levels of weaker acids were determined in this work. Undoubtedly, the discrepancy in results for weaker acids may be attributed to the much higher NIE yields for total acids (10.2 ± 0.5 wt %) obtained here versus their work (5.6 wt %).

TABLE 24. - HPLC subfractionation mass balances as a function of NIE procedure and total acid yield

Distillate	Cerro Negro	425-550° C	Wilmington	370-535°C	
NIE Run No.	1	3	7B	21D	21E ¹
Total acid yield, wt %	5.60	6.86	7.05	10.06	7.23
Distillate					
Subfraction yields, wt % total acids					
1	0.8	8.4	11	30	34
2	15	26	39	40	35
3	1.7	2.6	4	3	3
4	6.3	4	10	4	4
5	75.7	57	34	24	30
6	- ²	2	0.4	.1	1
Total	99.6	100	99	102	107
Subfraction yields, wt % distillate					
1	0.04	0.58	0.78	3.02	2.46
2	0.84	1.78	2.75	4.02	2.53
3	0.10	0.18	0.3	0.3	0.2
4	0.35	0.27	0.71	0.4	0.3
5	4.24	3.91	2.40	2.41	2.17
6	- ²	0.14	0.03	0.10	0.07
Total	5.57	6.86	7.00	10.2	7.7

¹Bases removed first; compare with run 21D results at left.

²Subfractions 5 and 6 were combined.

It should be noted that the significantly higher proportion of weaker and/or more hindered acids in concentrates obtained with the optimized versus earlier NIE methods places much higher demands on methodology for subsequent separation and analysis. For example, had the set of subfractions from the Cerro Negro 425-550° C run 1 acid concentrate (table 24) been used in the preceding section instead of those from the composited Wilmington acid concentrates, the apparent degree of class overlap between subfractions would have been significantly less. For Cerro Negro run 1 acids, the yield of subfraction 1, shown to be a troublesome mixture of highly hindered members of many classes in the case of Wilmington acids, was too small even to have warranted analysis. Similarly, elemental and IR analysis indicated cleaner partitioning of compound classes in the case of run 1 versus run 3 425-550° C Cerro Negro subfractions, simply because the compounds resulting in the

increased NIE total acid yield from run 1 to run 3 were by definition less acidic, more highly hindered, or otherwise more difficult to separate.

As discussed in Chapter 4, the main effect of reversing the normal order of the NIE columns to effect removal of bases before acids is to cause crossover of pyrrolic benzologs into the base concentrate. This effect is also demonstrated in table 24 by the decreased yield of subfraction 1 and especially subfraction 2 (whole distillate basis) from the acid concentrate obtained after base isolation, compared to the one obtained using the conventional order (acids removed first).

In conclusion, compounds which exhibited weak retention on ion exchange resins used for isolation of total acids typically also showed rapid elution during HPLC subfractionation. This finding is consistent with results in the previous section which indicated that structural effects on separation behavior over the NIE versus HPLC separations were similar. The higher acid and base fraction yields afforded by the optimized NIE method simplified the composition of the neutral fraction at the expense of increased complexity of acid and base fractions. Whole acid fractions from the optimized NIE procedure contain a much higher proportion of weak acids and atypically eluting members of more acidic classes which increase the difficulty of subsequent steps toward separation into compound classes.

Summary of Results for Cerro Negro Acid Fractions

Tables 25 and 26 show mass balances from representative subfractionations of Cerro Negro acid concentrates from distillates and residues, respectively. For the 425-550° C distillate, independent NIE and HPLC separations were performed using identical procedures to check their combined repeatability. Those results are shown in the second and third columns corresponding to the 425-550° C distillate (table 25). Very good agreement was obtained; the repeatability of both procedures is largely limited by the skill of the individual performing the gravimetric determination of fraction yields. Variations in subfraction yields for other sets of data in a given boiling range resulted from experimental modifications, as discussed below.

TABLE 25. - Mass balances from HPLC subfractionation of Cerro Negro acid concentrates from distillates

Distillate Boiling Range, ° C	200-425°C -----				425-550°C -----				550-700°C-----	
NIE Run No.	2	4	4	3	1	3	4	5	1	3
Total Acid Yield, Wt % Distillate	3.18	3.25	3.25	3.09	5.60	6.86	6.85	6.90	8.68	13.5
Subfraction Yields, Wt % Total Acids										
1	8.0	14.9 ²	8.8	8.3	0.8	8.4 ²	9.5 ²	15.0	1.0	29.3 ²
2	17.8	18.6	5.2	17.1	15.0	26	26	21.9	17.9	24
3	1.7	2.9	15.0	2.7	1.7	2.6	2.5	2.0	3.8	2.8
4	8.2	3.1	6.8	3.7	6.3	4.0	4.0	4.0	15.3	8.5
5	60.8	57.6	57.8	64.6	75.7	57	56	52.4	62.9	34
6	2.2	2.9	6.4	- ⁴	- ⁴	2.0	2.0	- ⁴	- ⁴	1.4
Total	98.7 ¹	(100)	100.0 ³	96.4 ⁵	99.6	(100)	(100)	95.3 ⁶	101.0	(100)
Subfraction Yields, Wt % Distillate										
1	0.24	0.48	0.29	0.26	0.04	0.58	0.65	1.04	0.09	3.96
2	0.57	0.60	0.17	0.53	0.84	1.78	1.78	1.51	1.55	3.24
3	0.05	0.09	0.49	0.08	0.10	0.18	0.17	0.14	0.33	0.38
4	0.26	0.10	0.22	0.11	0.35	0.27	0.27	0.28	1.33	1.15
5	1.93	1.87	1.88	2.00	4.24	3.91	3.84	3.62	5.46	4.59
6	0.07	0.09	0.20	- ⁴	- ⁴	0.14	0.14	- ⁴	- ⁴	0.19
Total	3.12	3.24	3.25	2.98	5.57	6.86	6.85	6.59	8.76	13.5

¹See figure 4.

²Subfraction yield by difference.

³Obtained using current conditions, see figure 6.

⁴Subfractions 5 and 6 were combined.

⁵Obtained using CHCl₃-based mobile phase, see figure 28.

⁶Obtained using CHCl₃-based mobile phase.

TABLE 26. - Mass balances from HPLC subfractionation of acid concentrates from distillation residues

Residue NIE Run No. Acid Concentrate	Cerro Negro >700°C 5+6			Wilmington >675°C ^{1,2} 2+3		Mayan >625°C ² 2	
	Strong	Weak-I	Weak-II	Strong	Weak	Strong	Weak
Concentrate Yield, Wt % Residue	20.4	7.69	4.64	21.5	11.7	17.7	8.72
Subfraction Yields, Wt % Concentrate							
1	44.4	62.7	20.2	29.7	61.3	17.3	71.9
2	22.5	25.8	21.9	30.2	24.5	8.4	11.4
3	10.4	3.5	16.0	13.7	4.2	16.8	2.1
4	13.5	6.1	15.3	23.8	5.8	33.4	5.0
5	2.1	2.0	4.4	5.1	2.1	12.6	8.4
Total	92.9	100.0	(95.6) ³	102.5	97.9	88.5	98.8
Subfraction Yields, Wt % Residue							
1	9.1	4.8	0.9	6.4	7.2	3.1	6.3
2	4.6	2.0	1.0	6.5	2.9	1.5	1.0
3	2.1	0.3	0.7	2.9	0.5	3.0	0.2
4	2.8	0.5	0.7	5.1	0.7	5.9	0.4
5	0.4	0.1	0.2	1.1	0.3	2.2	0.7
Total	19.0	7.7	3.5	22.0	11.6	15.7	8.6

¹Residue from 14.2 °API gravity Wilmington crude discussed in Chapter 6.

²See table 3, Chapter 1, for physical properties of crude.

³Includes 17.8 wt % CHCl₃-insolubles.

The increased yield for subfractions 1 and 2 typically obtained from acid concentrates comprising larger percentages of a given distillate was discussed in the preceding section. In all probability, yields for early eluting subfractions from acid concentrates obtained with the optimized NIE procedure (e.g., 11.4 wt % total acids from the 425-550° C distillate) would be still higher than any shown in the tables. Variations in yields for subfractions from 200-425° C acids reflect adjustments in cutpoints and other experimental conditions. Only combined data for subfractions 5 and 6 are directly comparable for that boiling range. Subfraction yields from CHCl₃-versus MTBE-based HPLC systems (see tables 6 and 10) generally corresponded well.

A significantly more detailed comparison of mass balance data in table 25 than provided above would require extensive supporting analytical information; since, as shown in prior sections, a given subfraction typically contains multiple compound classes and a given class may be distributed over multiple subfractions. The available supporting analytical data are not generally sufficient for such a comparison, nor is it warranted from a practical standpoint. Inspection of the available data (largely elemental and IR) indicated relatively clean partitioning of carboxylic acids into subfractions 5 and 6 in all cases except subfractions from the 550-700° C distillate. Elution profiles for ArOH, pyrrolic benzologs, and amides were similar to those observed for Wilmington 370-535° C acids discussed earlier. Variations in yields of early eluting fractions with changing experimental conditions simply reflected the more or less arbitrary selection of cutpoints for their collection. Thus, none of the sets of subfractions for a given boiling range could be shown to be significantly better or worse than the others.

Experience obtained with the CHCl₃-based mobile phase (table 10) during separation of Cerro Negro distillates revealed significantly earlier elution of carboxylic acids than indicated by the pure compounds in the standard blend. Figure 28 shows example chromatograms of the standard and Cerro Negro 200-425° C acids. The cutpoint between subfractions 4 and 5 indicated in the figure was found to cause approximately one-half of the carboxylic acids present to partition into subfraction 4. Subfraction 4 was subsequently re-separated with an adjusted cutpoint coinciding with the retention time of 2-naphthol, instead of slightly behind it as shown in the figure. The corrected yields are indicated in table 25.

FIGURE 28. - HPLC chromatograms of the standard blend (table 7) and a Cerro Negro 200-425° C acid concentrate (NIE Run 3) obtained using the CHCl_3 -based mobile phase. See table 10 for experimental conditions and table 25 for subfraction yields. Compare with figures 4 and 6.

Figure 29 shows representative chromatograms from subfractionation of acid concentrates from the Cerro Negro >700° C residue. The chromatograms from separation of weak versus strong acid concentrates were surprisingly similar for Cerro Negro and other residues listed in table 26. The distribution of subfraction yields from weak versus strong acid concentrates indicated higher proportions of compounds eluting into subfractions 1 and 2 in the case of weak acid concentrates, as observed with separation of SRC-II >325 °C+ and Wilmington 370-535° C weak versus strong acids discussed earlier. However, one particularly surprising feature of the yield distributions from subfractionation of strong acid concentrates from all three residues shown, was the very low proportion of material eluting in the region (subfraction 5) anticipated to contain multifunctional acids. In contrast, as discussed in Chapter 4, strong base concentrates from residues typically contained significant proportions of strongly retained species which probably contained multiple basic functional groups. Potentially, portions of Cerro Negro and Mayan strong acids which were not recovered after subfractionation may have contained multiple acidic functional groups. However, on the whole, the retention of nondistillate acids was much lower than anticipated, with lower proportions of compounds eluting into higher number subfractions than observed for acids from most distillates.

Table 27 lists elemental composition determined for Cerro Negro >700° C subfractions. Heteroatom distributions over the subfractions varied less than observed for subfractions from distillates (compare with table 17)--probably because of a higher occurrence of heteroatoms in nonacidic functional groups. Generally, H/C ratio increased with subfraction number as observed for distillate acids. As noted earlier, relatively acidic functional groups such as the carboxylic group tend to be associated with relatively saturated hydrocarbon skeletons in most petroleums. As noted in Chapter 2, the extremely high oxygen content of the whole Cerro Negro weak acid-II concentrate, and for subfractions obtained here, may indicate contamination or alteration during isolation. The significant proportion of CHCl₃-insoluble material present in the whole concentrate (see table 26) also suggests contamination or alteration.

FIGURE 29. - HPLC chromatograms from subfractionation Cerro Negro $>700^{\circ}\text{C}$ weak-II and strong acids. See table 10 for experimental conditions and table 26 for subfraction yields. Chromatograms from subfractionation of the $>700^{\circ}\text{C}$ weak-I concentrate were similar to that shown for weak-II acids.

TABLE 27. - Elemental content of Cerro Negro >700°C acid subfractions

Acid Concentrate	Subfraction No.	C	H	H/C	N	S	O ²
Strong	1	79.87	7.90	1.179	1.74	3.58	6.91
	2	82.98	7.75	1.113	1.89	3.48	3.90
	3	81.69	7.94	1.158	1.76	3.46	5.15
	4	77.91	8.97	1.372	1.46	3.26	8.40
	5	75.62	8.79	1.385	1.12	3.35	11.12
Weak-I	1	82.60	9.11	1.314	1.15	3.57	3.57
	2	81.83	8.29	1.033	1.35	3.89	4.64
	3	81.26	8.22	1.205	1.44	3.59	5.49
	4	75.33	8.37	1.324	1.93	3.41	10.96
	5	76.02	8.56	1.342	1.19	2.92	11.31
Weak-II	1	80.56	9.26	1.370	0.87	2.64	6.67
	2	76.76	8.46	1.124	1.05	2.95	10.78
	3	76.11	8.32	1.303	1.08	2.77	11.72
	4	76.54	8.56	1.333	1.02	2.82	11.06
	5	65.44	8.61	1.568	1.94	1.77	22.44

¹Atomic ratio.²By difference.

The compositional complexity of and hydrogen bonding within subfractions from Cerro Negro or other residues caused their IR spectra to show little useful information except that subfraction 4 from strong acid concentrates typically showed carbonyl bands consistent with carboxyl groups. Also, the methods described in the appendices were not available at the time work on residue acids was carried out. Thus, the ineffectiveness of conventional IR analysis and lack of alternatives prevented further progress in this area. Given the complexity of subfractions from petroleum distillates, analysis of subfractions from residues would be extremely difficult even with the methods described in the appendices; however, it should be attempted in the future.

Figures 30-38 illustrate preliminary results from study of the relationship of nitrogen- and sulfur-containing compounds versus total (N-, S-, and O-containing) species in a series of subfractions from the 200-425° C distillate. The objective was to determine the probable forms (functional groups) of sulfur and nitrogen present. The predominance of pyrrolic nitrogen types in subfractions 1 and 2 is indicated by the correspondence of N versus FID traces in figures 30 and 31. Sulfur is most abundant in higher boiling members of those subfractions; the low overall intensity of the S-detector trace suggests only partial elution of S-containing compounds.

FIGURE 30. - GC analysis of Cerro Negro 200-425° C acid subfraction 1 with three-way detection. Note the higher apparent boiling range of S-containing compounds compared to N-containing or total (FID) components present.

FIGURE 31. - GC analysis of Cerro Negro 200-425° C acid subfraction 2 with three-way detection. Note the predominance of N-containing compounds indicated by the correspondence of N vs. FID detector traces. The two humps approximately correspond to carbazole and benzocarbazole homologs, respectively.

FIGURE 32. - GC analysis of Cerro Negro 200-425° C acid subfraction 3 with three-way detection. N-containing components (benzo[c]carbazole homologs) comprise a relatively minor proportion of the fraction (compare N vs. FID trace); ArOH predominate.

FIGURE 33. - GC analysis of Cerro Negro 200-425° C acid subfraction 4 (predominantly ArOH) with three-way detection. The correlation between FID and S detector traces indicates significant quantities of S-containing ArOH, e.g., hydroxybenzothiophene homologs.

FIGURE 34. - GC analysis of Cerro Negro 200-425° C acid subfraction 5 with three-way detection. Compare with figure 35.

FIGURE 35. - GC analysis of esterified Cerro Negro 200-425° C acid subfraction 5 with three-way detection. Note the overall (FID) increase in volatility after esterification and especially that of sulfur-containing compounds (see figure 34). The two distinct peaks eluting at ca. 33 and 37 min. were identified as tricyclic terpenoid carboxylic acids (28).

FIGURE 36. - GC analysis of Cerro Negro 200-425° C acid subfraction 6 with three-way detection. Note the prominent S-detector response relative to that of the FID. Compare with figure 37.

FIGURE 37.-- GC analysis of esterified Cerro-Negro 200-425° C acid subfraction 6 with three-way detection. Compare with figure 36; note the increased N-detector response after esterification.

FIGURE 38. - GC analysis of whole Cerro Negro 200-425° C acids.
Compare with figures 30-37.

The predominance of ArOH in subfractions 3 and 4 is apparent in the poor correlation between N versus FID traces in figures 32 and 33, compared to that in figures 30 and 31, and the low overall intensity of the N-detector trace in figure 33. However, amide-forms of nitrogen may not have been eluted from the GC-column, based on prior literature work cited in the Introduction. The increased intensity of the S-detector traces evident for subfractions 3 and 4, and their greater correspondence with the FID trace, compared to that observed for subfractions 1 and 2, suggests presence of hydroxylated thiophenic types or other S-containing species. Hydroxylated thiophenic compounds have been identified in an SRC-II coal liquid (145).

Comparison of results for subfraction 5 before and after conversion to methyl esters (figures 34 and 35) indicates significant quantities of thiophenic and/or other types of sulfur compounds substituted with carboxyl groups. The S-detector trace in figure 35 shows significantly greater intensity and correlation with the FID trace than observed in figure 34. The significant shift in the FID trace of the esterified subfraction to lower boiling ranges indicates a predominance of carboxyl-substituted compounds, in accordance with IR and NAT results. The low elemental nitrogen content of this subfraction (0.13 wt %) is reflected in the low intensity of the N-detector traces in either figure.

An analogous comparison of GC chromatograms of plain versus esterified subfraction 6 (figures 36 and 37) revealed a smaller relative effect on the S-detector trace but a much larger enhancement of the N-detector signal after conversion to methyl esters. The latter observation is consistent with significant quantities of carboxyl-substituted nitrogen compounds in this subfraction.

The detector traces in figure 38 for the whole acid concentrate largely reflect features evident in traces for subfractions 1, 2, and 5 because they comprise much higher proportions of the total acids than the other subfractions (see table 25, second set of data for 200-425° C acids).

One feature readily apparent in all of the figures is the much lower number of resolved GC peaks than observed for the SRC-II subfractions; for example see figure 10. This feature reflects the much higher complexity of petroleum-derived fractions. GC/MS measurements of individual acidic compounds in Cerro Negro acid fractions have ranged from a high (whole

distillate basis) of 160 ppm for the single most prominent acidic compound in the 425-550° C distillate (a tricyclic terpenoid carboxylic acid, see ref. 28) to a low of 0.16 ppm (4-ethylphenol in the 200-425° C distillate, see ref. 146). In any case, these results indicate on the order of 10^5 - 10^7 components in acid fractions from distillates, which themselves comprise less than 10% of the total distillate. This estimate puts the magnitude of work required for "comprehensive analysis" of Cerro Negro heavy oil in proper perspective.

HR/MS and GC/MS analyses of 200-425° C acid subfractions were initiated, but data interpretation is incomplete at the time of writing. As noted above, the degree of effort required and volume of data generated from this work would dwarf that from the SRC-II subfractions discussed earlier.

In conclusion, subfractionation of Cerro Negro acid concentrates obtained using prototype NIE procedures have been completed for all boiling ranges >200° C. Analysis of the resulting subfractions is substantially incomplete, due to the unavailability of appropriate methods of analysis at the time the separation work was performed. Application of the methods described in the appendices--and potentially, development of additional methods--to the available subfractions, or new ones generated using current separation methodology, is needed to obtain more complete data on composition of Cerro Negro acids.

CONCLUSIONS

Development of instrumental methods for determination of acidic functional groups, and in selected cases individual acidic compounds, has progressed to the point where subfractionation of whole acid concentrates is no longer required or even desired. The NMR method described in Appendix 2 appears to be the best available general approach for functional group analysis. On the other hand, there is an inherent danger in simplified approaches based only on functional groups for description of acidic compounds in petroleum or syncrudes. For example, do ArOH in subfraction 1 behave chemically in the same manner as those in subfraction 4? They certainly do not in the case of the HPLC subfractionation. Although the hypothesis has not yet been investigated in detail, it is quite possible that HPLC separation behavior is a better indicator of common chemical properties than conventional functional group classifications.

This report has examined the performance of the HPLC subfractionation method more critically and in greater detail than perhaps any other petroleum separation method ever reported in the open literature. If anything, it has been overzealous in reporting its deficiencies and deficient in emphasizing its strengths. For example, in recent applications toward separation of acids from kerosene and diesel boiling ranges, subfractions anticipated to contain pyrrolic benzologs, ArOH, and other classes did in fact contain those types at purities exceeding 90% in some cases. However, results presented here for gas oil and higher boiling ranges indicating substantial class overlap are typical. This relevant question is: is it possible to reduce class overlap in separation of higher boiling fractions? One possible approach would be to add another dimension to the separation scheme (subsubfractions). Obviously, tradeoffs between additional information obtained versus the extra effort involved would have to be considered.

Further development of analytical methods will be required to obtain adequate analyses of acidic multifunctional/multiheteroatom compounds or compound types, amides, and trace acidic components apparently responsible for thermal and storage instability in distillate fuels. Although some progress has been made here and in other laboratories, the present methodology remains inadequate for the above.

The complexity of nondistillable acids is sufficiently great that simple classifications such as "carboxylic acids," "pyrrolic benzologs," etc. (maybe even "acids") are inadequate and even misleading. Given the significant number of heteroatoms (including metals) present per average molecule (see Chapter 2), an alternate means of describing and classifying them should be devised. This need is apparent even in the rudimentary data presented here, which indicated very similar elemental composition for compounds in weak versus strong acid concentrates or any of the various subfractions.

On the other hand, distillate acids, including those from Cerro Negro, may be adequately described in terms of relatively few classes or types: thiols, hydroxyl compounds, benzologs of pyrrole, amides, and carboxylic acids. However, the structural range within each class indicated by the present work is quite large, more so than apparent in most earlier studies. Also, the proportion of multiheteroatomic species in distillates is significant; e.g., Wilmington 370-535° C acids contain an average of 1.4 heteroatoms per molecule.

The class most easily separated by liquid chromatography, including the procedure discussed here, is carboxylic acids. In the described method, weaker acidic classes elute before carboxylic acids in order of their relative acidities. However, steric hindrance, intramolecular bonding, inductive, and other structural effects can significantly alter separation behavior of a given compound relative to the bulk of the compounds in its class. Those effects generally increase with the boiling range, causing greater class-overlap in separations of higher boiling acid concentrates.

REFERENCES

1. Dooley, J. E., D. E. Hirsch, and C. J. Thompson. *Hydroc. Process.*, v. 53, No. 7, 1974, p. 141.
2. McKay, J. F., T. E. Cogswell, J. H. Weber, and D. R. Latham. *Fuel*, v. 54, 1975, p. 50.
3. McKay, J. F., J. H. Weber, and D. R. Latham. *Anal. Chem.*, v. 48, 1976, p. 891.
4. McKay, J. F., P. J. Amend, P. M. Harnsberger, T. E. Cogswell, and D. R. Latham. *Fuel*, v. 60, 1981, p. 14.
5. McKay, J. F., P. M. Harnsberger, R. B. Erickson, T. E. Cogswell, and D. R. Latham. *Fuel*, v. 60, 1981, p. 17.
6. McKay, J. F., D. R. Latham, and W. E. Haines. *Fuel*, v. 60, 1981, p. 27.
7. Snyder, L. R. *Acc. Chem. Res.*, v. 3, 1970, p. 290.
8. Snyder, L. R. *Anal. Chem.*, v. 41, 1969, p. 314.
9. Snyder, L. R., B. E. Buell, H. E. Howard. *Anal. Chem.*, v. 40, 1968, p. 1303.
10. Snyder, L. R. *Anal. Chem.*, v. 41, 1969, p. 1084.
11. Lochte, H. L., and E. R. Littman. *The Petroleum Acids and Bases*, Chemical Publishing Co., New York, NY, 1955, pp. 9-278.
12. Seifert, W. K. *Progress in the Chemistry of Organic Natural Products*, v. 32, W. Herz, H. Grisebach, and G. W. Kirby (Eds.), Springer-Verlag, New York, NY, 1975, pp. 1-49.
13. Teeter, R. M. *Anal. Chem.*, v. 39, 1967, p. 1742.
14. Seifert, W. K., and W. G. Howells. *Anal. Chem.*, v. 41, 1969, p. 554.
15. Seifert, W. K. *Anal. Chem.*, v. 41, 1969, p. 562.
16. Seifert, W. K., and R. M. Teeter. *Anal. Chem.*, v. 41, 1969, p. 786.
17. Seifert, W. K., R. M. Teeter, W. G. Howells, and M. J. R. Cantow. *Anal. Chem.*, v. 41, 1969, p. 1638.
18. Seifert, W. K., and R. M. Teeter. *Anal. Chem.*, v. 42, 1970, p. 180.
19. Seifert, W. K., and R. M. Teeter. *Anal. Chem.*, v. 42, 1970, p. 750.
20. Seifert, W. K., E. J. Gallegos, and R. M. Teeter. *J. Am. Chem. Soc.*, v. 94, 1972, p. 5880.

21. Cyr, T. D., and O. P. Strausz. *J. Chem. Soc., Chem. Commun.*, 1983, p. 1028.
22. Payzant, J. D., A. M. Hogg, D. S. Montgomery, and O. P. Strausz. *AOSTRA J. Res.*, v. 1, 1985, p. 203.
23. Schmitter, J.-M., P. Arpino, and G. Guiochon. *J. Chromatogr.*, v. 167, 1978, p. 149.
24. Douglas, A. G., M. Blumer, G. Eglinton, and K. Douraghi-Zadeh. *Tetrahedron*, v. 27, 1971, p. 1071.
25. Chong, S.-L., and J. F. McKay. *Fuel*, v. 63, 1984, p. 303.
26. Ocampo, R., H. J. Callot, and P. Albrecht. *J. Chem. Soc., Chem. Commun.*, 1985, p. 198.
27. Ocampo, R., H. J. Callot, and P. Albrecht. *J. Chem. Soc., Chem. Commun.*, 1985, p. 200.
28. Green, J. B., B. K. Stierwalt, J. S. Thomson, and C. A. Treese. *Anal. Chem.*, v. 57, 1985, p. 2207.
29. E. J. Gallegos. *J. Chromatogr. Sci.*, v. 25, 1987, p. 296.
30. Dzidic, I., A. C. Somerville, J. C. Raia, and H. V. Hart. *Anal. Chem.*, v. 60, 1988, p. 1318.
31. Payzant, J. D., T. W. Mojelsky, T. D. Cyr, D. S. Montgomery, and O. P. Strausz. *Org. Geochem.*, v. 8, 1985, p. 177.
32. Dadey, E. J., S. L. Smith, and B. H. Davis. *Energy Fuels*, v. 2, 1988, p. 326.
33. Green, J. B., C. A. Treese, S. K.-T. Yu, J. S. Thomson, C. P. Renaudo, and B. K. Stierwalt. *Am. Chem. Soc., Div. Fuel Chem. Prepr.*, v. 31, No. 2, 1986, p. 126.
34. Sauer, R. W., F. W. Melpolder, and R. A. Brown. *Ind. Eng. Chem.*, v. 44, 1952, p. 2606.
35. Hartung, G. K., and D. M. Jewell. *Anal. Chim. Acta*, v. 26, 1962, p. 514.
36. Snyder, L. R., and B. E. Buell. *Anal. Chem.*, v. 36, 1964, p. 767.
37. Dorbon, M., J.-M. Schmitter, P. Arpino, and G. Guiochon. *J. Chromatogr.*, v. 246, 1982, p. 255.
38. Dorbon, M., J.-M. Schmitter, P. Garrigues, I. Ignatiadis, M. Ewald, P. Arpino, and G. Guiochon. *Org. Geochem.*, v. 7, 1984, p. 111.
39. Dorbon, M., I. Ignatiadis, J.-M. Schmitter, P. Arpino, G. Guiochon, H. Toulhoat, and A. Huc. *Fuel*, v. 63, 1984, p. 565.

40. Ignatiadis, I., P. Arpino, and M. Dorbon. *Rev. Inst. Fran. Petrol.*, v. 41, 1986, p. 551.
41. Frakman, Z., T. M. Ignasiak, D. S. Montgomery, and O. P. Strausz. *AOSTRA J. Res.*, v. 3, 1987, p. 131.
42. Sturm, G. P., Jr., J. B. Green, S. Y. Tang, J. W. Reynolds, and S. K.-T. Yu. *Am. Chem. Soc., Div. Petrol. Chem. Prepr.*, v. 32, 1987, p. 369.
43. Sturm, G. P., Jr., J. B. Green, R. D. Grigsby, F. L. Tilley, J. W. Reynolds, and S. K.-T. Yu. *Am. Chem. Soc., Div. Petrol. Chem. Prepr.*, v. 34, 1989, p. 367.
44. Schmitter, J.-M., and P. Arpino. *Mass Spectrom. Rev.*, v. 4, 1985, p. 87.
45. Yoshida, T., P. D. Chantal, and H. Sawatzky. *Am. Chem. Soc., Div. Petrol. Chem. Prepr.*, v. 33, 1988, p. 341.
46. Bett, G., T. G. Harvey, T. W. Matheson, and K. C. Pratt. *Fuel*, v. 62, 1983, p. 1445.
47. Novotny, M., J. W. Strand, S. L. Smith, D. Wiesler, and F. J. Schwende. *Fuel*, v. 60, 1981, p. 213.
48. Later, D. W., R. B. Lucke, E. K. Chess, and J. A. Franz. *Fuel*, v. 66, 1987, p. 1347.
49. Ford, C. D., S. A. Holmes, L. F. Thompson, and D. R. Latham. *Anal. Chem.*, v. 53, p. 831.
50. Holmes, S. A., and L. F. Thompson. *Fuel*, v. 62, 1983, p. 709.
51. Holmes, S. A. *AOSTRA J. Res.*, v. 2, 1986, p. 167.
52. Bünge, J. W. *Shale Oil, Tar Sands, and Related Fuel Sources*, T. F. Yen (Ed.), *Adv. Chem. Ser. No. 151*, Am. Chem. Soc., Wash., DC, 1976, Chapter 10.
53. Bünge, J. W., K. P. Thomas, and S. M. Dorrence. *Fuel*, v. 58, 1979, p. 183.
54. Jacobson, J. M., and M. R. Gray. *Fuel*, v. 66, 1987, p. 749.
55. Copelin, E. C. *Anal. Chem.*, v. 36, 1964, p. 2274.
56. Rall, H. T., C. J. Thompson, H. J. Coleman, and R. L. Hopkins. *Sulfur Compounds in Crude Oil*, U.S. Bur. Mines Bull. 659, 1972, 187 pp.
57. Saetre, R., and A. Somogyvari. *Am. Chem. Soc., Div. Petrol. Chem. Prepr.*, v. 34, 1989, p. 268.
58. Gutzeit, J. *Oil Gas J.*, April 5, 1976, p. 156.

59. Bhan, O. K., J. B. Green, and D. W. Brinkman. Am. Chem. Soc., Div. Petrol. Chem. Prepr., v. 32, 1987, p. 361.
60. Thakkar, V. P., R. M. Baldwin, and R. L. Bain. Fuel Process. Technol., v. 4, 1981, p. 235.
61. Scheppele, S. E., G. J. Greenwood, R. J. Pancirov, and T. R. Ashe. Upgrading Coal Liquids, R. F. Sullivan (Ed.), Adv. Chem. Ser. 156, Am. Chem. Soc., Wash., DC, 1981, Chapter 2.
62. Dzidic, I., M. D. Balicki, and H. V. Hart. Fuel, v. 67, 1988, p. 1155.
63. Pedley, J. F., R. W. Hiley, and R. A. Hancock. Fuel, v. 66, 1987, p. 1646.
64. Hiley, R. W., and J. F. Pedley. Fuel, v. 67, 1988, p. 469.
65. Pedley, J. F., R. W. Hiley, and R. A. Hancock. Fuel, v. 67, 1988, p. 1125.
66. Pedley, J. F., R. W. Hiley, and R. A. Hancock. Fuel, v. 68, 1989, p. 27.
67. Hazlett, R. N., and G. Kelso. Proc. 2nd Int. Conf. on Long-Term Storage Stabilities of Liquid Fuels, L. L. Stavinoha (Ed.), Southwest Research Institute, San Antonio, TX, 1986, p. 541.
68. Pearson, C. D., and J. B. Green. Fuel, v. 68, 1989, p. 456.
69. Wright, C. W., E. K. Chess, D. J. Hendren, D. L. Stewart, D. D. Mahlum, and B. W. Wilson. Fuel, v. 67, 1988, p. 1283.
70. White, C. M., L. Jones, and N. C. Li. Fuel, v. 62, 1983, p. 1397.
71. Hazlett, R. N., and A. J. Power. Proc. 2nd Int. Conf. on Long-Term Storage Stabilities of Liquid Fuels, L. L. Stavinoha (Ed.), Southwest Research Institute, San Antonio, TX, 1986, p. 556.
72. Bhan, O. K., D. W. Brinkman, J. B. Green, and B. Carley. Fuel, v. 66, 1987, p. 1200.
73. Coordinating Research Council. Handbook of Aviation Fuel Properties, SAE, Inc., Warrendale, PA, 1983.
74. Boldt, K., and B. R. Hall. Significance of Tests for Petroleum Products, ASTM Special Technical Publication 7C, ASTM, Philadelphia, PA, 1977.
75. Clark, R. H., and L. Smith. 3rd International Conference on Stability and Handling of Liquid Fuels, London, UK, 1988, paper no. 46.
76. Steele, W. V., R. D. Chirico, and S. E. Knipmeyer. The Use of a Differential Scanning Calorimeter in Jet Fuel Thermal Stability Studies. NIPER Topical Report in preparation.

77. Galya, L. G., D. C. Cronauer, P. C. Painter, and N. C. Li. Ind. Eng. Chem. Fundam., v. 25, 1986, p. 129.
78. Black, B. H., and D. R. Hardy. Am. Chem. Soc., Div. Fuel Chem. Prepr., v. 34(2), 1989, p. 573 and 581.
79. Fodor, G. E., D. W. Naegeli, and K. B. Kohl. Energy Fuels, v. 2, 1988, p. 729.
80. Cogswell, T. E., J. F. McKay, and D. R. Latham. Anal. Chem., v. 43, 1971, p. 645.
81. McKay, J. F., D. M. Jewell, and D. R. Latham. Separation Sci., v. 7, 1972, p. 361.
82. Snyder, L. R., and B. E. Buell. Anal. Chem., v. 40, 1968, p. 1295.
83. Snyder, L. R., and B. E. Buell. J. Chem. Eng. Data, v. 11, 1966, p. 545.
84. Snyder, L. R., and D. L. Saunders. Chromatography in Petroleum Analysis, K. H. Altgelt and T. H. Gouw (Eds.), M. Dekker, New York, NY, 1979, Chapter 10.
85. Green, J. B. J. Chromatogr., v. 209, 1981, p. 211.
86. Pazant, J. D., A. M. Hogg, D. S. Montgomery, and O. P. Strausz. AOSTRA J. Res., v. 1, 1985, p. 175.
87. Matsunaga, A., and S. Kusayanagi. Am. Chem. Soc., Div. Fuel Chem. Prepr., v. 26, No. 2, 1981, p. 59.
88. Matsumaga, A. Anal. Chem., v. 55, 1983, p. 1375.
89. Ruckmick, S. C., and R. J. Hurtubise. J. Chromatogr., v. 321, 1985, p. 343.
90. Ruckmick, S. C., and R. J. Hurtubise. J. Chromatogr., v. 331, 1985, p. 55.
91. Green, J. B., and P. L. Grizzle. Trace Analysis, v. 2, J. F. Lawrence (Ed.), Academic P., New York, NY, 1982, pp. 223-265.
92. Callmer, K., L.-E. Edholm, and B. E. F. Smith. J. Chromatogr., v. 136, 1977, p. 45.
93. Schabron, J. F., R. J. Hurtubise, and H. F. Silver. Anal. Chem., v. 50, 1978, p. 1911.
94. Ogan, K., and E. Katz. Anal. Chem., v. 53, 1981, p. 160.
95. Wittmann, S., Z. Decsy, S. Regensperger, and E. Pudmer. Anal. Chem., v. 56, 1984, p. 989.

96. Dean, J. A. (Ed.). *Lange's Handbook of Chemistry*, 13th Edition, McGraw-Hill, New York, NY, 1985, pp. (5-18)-(5-70).
97. Albert, A. *Physical Methods in Heterocyclic Chemistry*, v. 1, A. R. Katritzky (Ed.), Academic Press, New York, NY, 1963, pp. 1-108.
98. Ross, A. M., D. L. Whalen, S. Eldin, and R. M. Pollack. *J. Am. Chem. Soc.*, v. 110, 1988, p. 1981.
99. Keefte, J. R., A. J. Kresge, and Y. Yin. *J. Am. Chem. Soc.*, v. 110, 1988, p. 1982.
100. Bordwell, F. G. *Acc. Chem. Res.*, v. 21, 1988, p. 456.
101. Green, J. B., and R. J. Hoff. *J. Chromatogr.*, v. 209, 1981, p. 231.
102. Green, J. B. *J. Chromatogr.*, v. 358, 1986, p. 53.
103. Green, J. B., J. S. Thomson, S. K.-T. Yu, C. A. Treese, B. K. Stierwalt, and C. P. Renaudo. *Am. Chem. Soc., Div. Fuel Chem. Prepr.*, v. 31, No. 1, 1986, p. 198.
104. Green, J. B., B. K. Stierwalt, J. A. Green, and P. L. Grizzle. *Fuel*, v. 64, 1985, p. 1571.
105. Chmielowiec, J. *Anal. Chem.*, v. 55, 1983, p. 2367.
106. Ruckmick, S. C., R. J. Hurtubise, and H. F. Silver. *J. Chromatogr.*, v. 392, 1987, p. 277.
107. Snyder, L. R. *Principles of Adsorption Chromatography*, M. Dekker, New York, NY, 1968.
108. Stalling, D. L., J. D. Petty, and L. M. Smith. *J. Chromatogr. Sci.*, v. 19, 1981, p. 18.
109. Snyder, L. R., and J. J. Kirkland. *Introduction to Modern Liquid Chromatography*, 2nd ed., J. Wiley and Sons, New York, NY, 1979.
110. Vogh, J. W., and J. S. Thomson. *Anal. Chem.*, v. 53, 1981, p. 1345.
111. Bradley, C., and J. W. Carnahan. *Anal. Chem.*, v. 60, 1988, p. 858.
112. Woolsey, N., R. Baltisberger, K. Klabunde, V. Stenberg, and R. Kaba. *Am. Chem. Soc., Div. Fuel Chem. Prepr.*, v. 21, No. 7, 1976, p. 33.
113. Bockrath, B. C., R. B. LaCount, and R. P. Noceti. *Fuel*, v. 59, 1980, p. 621.
114. Dutta, P. K., and R. J. Holland. *Fuel*, v. 62, 1983, p. 732.
115. Nakajima, T., and C. Tanobe. *J. Inst. Petrol. (London)*, v. 59, 1973, p. 32.

116. Dutta, P. K., and R. J. Holland. *Fuel*, v. 63, 1984, p. 197.
117. Hartung, G. K., D. M. Jewell, O. A. Larson, and R. A. Flinn. *J. Chem. Eng. Data*, v. 6, 1961, p. 477.
118. Zanella, I., J. V. Weber, R. Gruber, and D. Cagniant. *Fuel Process. Technol.*, v. 20, 1988, p. 33.
119. Wood, K. V., L. F. Albright, J. S. Brodbelt, and R. G. Cooks. *Anal. Chim. Acta*, v. 173, 1985, p. 117.
120. Buchanan, M. V. *Anal. Chem.*, v. 56, 1984, p. 546.
121. Olson, E. S., and J. W. Diehl. *Anal. Chem.*, v. 59, 1987, p. 443.
122. Buchanan, M. V. *Anal. Chem.*, v. 54, 1982, p. 570.
123. Bender, A. O., T. M. Sarkissian, and A. M. Allawi. *Fuel*, v. 68, 1989, p. 607.
124. Dietz, W. A. *J. Chromatogr. Sci.*, v. 10, 1972, p. 423.
125. Brady, R. F., Jr., and B. C. Pettitt. *J. Chromatogr.*, v. 93, 1974, p. 375.
126. Husain, S., P. Kunzelmann, and H. Schildknecht. *J. Chromatogr.*, v. 137, 1977, p. 53.
127. Macak, J., P. Buryan, and J. Hrivnak. *J. Chromatogr.*, v. 89, 1974, p. 309.
128. Buryan, P., J. Macak, and J. Hrivnak. *J. Chromatogr.*, v. 137, 1977, p. 425.
129. Buryan, P., and J. Macak. *J. Chromatogr.*, v. 139, 1977, p. 69.
130. Buryan, P., J. Macak, and V. M. Nabivack. *J. Chromatogr.*, v. 148, 1978, p. 203.
131. Buryan, P., and J. Macak. *J. Chromatogr.*, v. 150, 1978, p. 246.
132. Guenther, F. R., R. M. Parris, S. N. Chesler, and L. R. Hilpert. *J. Chromatogr.*, v. 207, 1981, p. 256.
133. White, C. M., and N. C. Li. *Anal. Chem.*, v. 54, 1982, p. 1564 and 1570.
134. Nakazawa, T., M. Kuroki, and Y. Tsunashima. *J. Chromatogr.*, v. 211, 1981, p. 388.
135. Vassilaros, D. L., M. Kong, D. W. Later, and M. L. Lee. *J. Chromatogr.*, v. 252, 1982, p. 1.

136. Wright, C. W., D. W. Later, and B. W. Wilson. J. High Resolut. Chromatogr. Chromatogr. Commun., v. 8, 1985, p. 283.
137. Green, J. B., C. A. Treese, and S. K.-T. Yu. Chemical/Physical Separations of Alternate Petroleum Distillates. III. HPLC Subfractionation of Distillate Acids. NIPER Topical Report No. 42, 1985, 26 pp.
138. Sturm, G. P., Jr., J. B. Green, S. Y. Tang, J. W. Reynolds, and S. K.-T. Yu. Detailed Analysis of Polar Compounds in Wilmington Gas Oil and Hydrotreated Products. NIPER Topical Report No. 152, 1986, 63 pp.
139. Rafii, E., R. Faure, L. Lena, E.-J. Vincent, and J. Metzger. Anal. Chem., v. 57, 1985, p. 2854.
140. Harrison, R. H., S. E. Scheppele, G. P. Sturm, Jr., and P. L. Grizzle. J. Chem. Eng. Data, v. 30, 1985, p. 183.
141. Sutterfield, D. S., W. C. Lanning, and R. E. Royer. Upgrading Coal Liquids, R. F. Sullivan (Ed.), Adv. Chem. Ser. 156, Am. Chem. Soc., Wash., DC, 1981, Chapter 5.
142. Rostad, C. E., and W. E. Pereira. J. High Resolut. Chromatogr. Chromatogr. Commun., v. 9, 1986, p. 328.
143. Jewell, D. M., J. H. Weber, J. W. Bunger, H. Plancher, and D. R. Latham. Anal. Chem., v. 44, 1972, p. 1391.
144. Green, J. B., R. J. Hoff, P. W. Woodward, and L. L. Stevens. Fuel, v. 63, 1984, p. 1290.
145. Nishioka, M., M. L. Lee, H. Kudo, D. R. Muchiri, L. J. Baldwin, S. Pakray, J. G. Stuart, and R. N. Castle. Anal. Chem., v. 57, 1985, p. 1327.
146. Project BFR2 Quarterly Report for April 1-June 30, 1987. NIPER Report No. 268, August 1987, pp. 119-133.

APPENDIX 1

INFRARED-CHEMICAL DERIVATIZATION METHOD FOR DETERMINATION OF TOTAL HYDROXYLS AND CARBOXYLS IN PETROLEUM AND SYNCRUDES

APPENDIX 1

INFRARED-CHEMICAL DERIVATIZATION METHOD FOR DETERMINATION OF TOTAL HYDROXYLS AND CARBOXYLS IN PETROLEUM AND SYNCRUDES

by

Shirley K.-T. Yu and John B. Green

ABSTRACT

Oxygen-containing functional groups (hydroxyl and carboxyl) in fuels or crude oils, or fractions thereof, are determined by IR spectroscopy. The approach is based on chemical derivatization followed by measurement of IR bands of the corresponding derivatives. The chemical derivatization procedure involves two steps: 1) esterification of carboxylic acids with 2,2,2-trifluoroethanol and 2) acylation of alcoholic and phenolic hydroxyls with trifluoroacetyl chloride. The aryl trifluoroacetates absorb at 1800 cm^{-1} ; the 2,2,2-trifluoroethyl esters absorb in the region $1760\text{--}1740\text{ cm}^{-1}$. Variation of molar absorptivity of the derivatives as a function of structure is determined using pure compounds and well defined fractions from actual fuel samples. The overall accuracy, precision, sensitivity, and range of applicability to petroleum and related sample types are discussed.

INTRODUCTION

Chemical derivatization has traditionally been an important organic analytical tool for increasing specificity and sensitivity in the determination of functional groups, compound classes, or individual compounds. In functional group analysis of fuels or petroleum, the typical derivatization approach involves addition of an element or chemical functionality which is absent or present in low abundance, followed by instrumental determination of the introduced element or moiety. The concentration of the added element or moiety is then used to calculate the parent functional group concentration from the stoichiometry of the reaction, with correction for reaction yield in cases of nonquantitative conversion or where losses during product workup occur. For example, ^{19}F NMR was used to determine trifluoroacetyl derivatives

of hydroxyaromatics, alcohols, thiols, and amines (1-5)*. Similarly, ^{119}Sn NMR has been used to measure hydroxyaromatics in coal liquids reacted with bis (tri-*n*-butyltin) oxide (6), and ^{29}Si NMR has been used in conjunction with silyating agents (7). A variety of wet chemical methods based on acylation followed by determination of excess acylating agent (8) or hydrolysis and subsequent analysis of acetic or trifluoroacetic acid (9,10) is also available. Results from the latter are typically expressed as total acylatable compounds or in an equivalent manner.

Infrared (IR) spectroscopy in conjunction with chemical derivatization has also been used for functional group determination. Several researchers (11-14) have used acylation techniques for quantitative measurement of hydroxyl content of coals and bitumen. They employed acetic anhydride as the derivatizing agent and measured the band from the resulting acetate esters at $1745\text{--}1770\text{ cm}^{-1}$. Since unaltered coal and other fossil fuels (15) typically exhibit significant absorption in that IR region, precise background subtraction to determine net absorption by the acetate derivatives is required. However, measurement of underivatized hydroxyls ($3600\text{--}3800\text{ cm}^{-1}$) suffers from even greater disadvantages. For example, Osawa and Shih (16) state that OH band intensity is significantly affected by moisture in coal. Therefore, semi-quantitative information is obtained only after rigorous drying of the powdered coal, potassium bromide, and of the resulting KBr pellets. Robbins, et al. (17) point out the possibility of N-H band interference in the determination of hydroxyl content of coal liquids dissolved in tetrahydrofuran. In addition, the frequency, shape, and intensity of OH bands are significantly affected by hydrogen bonding, including interactions involving absorbed water (10,18,19).

The IR spectra of underivatized carboxylic acids in methylene chloride exhibit bands corresponding to monomeric and dimeric species. The carbonyl absorption of the dimeric species occurs at ca. 1710 cm^{-1} ; the monomer (free acid) band appears at ca. 1750 cm^{-1} . Helm and Peterson (20) found the equilibrium ratio of monomer and dimer as determined by IR to be both solvent dependent and affected by other hydrogen bonding species present. Cogswell,

*Underlined numbers in parentheses refer to items in the list of references at the end of this appendix.

et al. (21) utilized this distinctive two band pattern for qualitative analysis for carboxylic acids in petroleum acid concentrates. Later, McKay, et al. (22) used an average molar absorptivity obtained from pure compounds for quantitative determination of carboxylic acids in petroleum acid concentrates and pure carboxylic acid fractions. In selected cases, they used tetrahydrofuran as the solvent in order to eliminate the interference from the molecular association between carboxylic acids and amides. Bunger, et al. (23) found significant overlap in carbonyl bands from carboxylic acids, ketones, and esters in tar sand bitumens. Liotta, et al. (24) state that free carboxylic acid groups are difficult to detect in IR spectra of coals, but are easily detected after methylation. In general, esterification of carboxylic acids with aliphatic alcohols results in esters with absorption at ca. 1720 cm^{-1} (25).

Several methods for esterification of carboxylic acids (26-32) have been reported. Acylation is normally carried out using the corresponding acid anhydride or chloride (33). However, the majority of these procedures are not well suited for IR applications because either the solvent system, residual reagents, or reaction by-products produce significant background absorption in the IR regions of interest. Basic requirements for chemical derivatization procedures for IR include use of solvents with high IR transparency, quantitative product yields, and suitability for microscale reactions. Since halogenated derivatives frequently exhibit bands at significantly higher wavenumbers than nonhalogenated compounds (34), fluorinated acylating or esterifying agents seemed a logical choice for reducing the likelihood of interference in a halogen-free matrix such as petroleum. The overall reaction scheme:

shown using p-hydroxybenzoic acid as an example was assimilated from prior work on esterification of carboxylic acids in trifluoroacetic anhydride media (27-31), and acylation of hydroxyl groups with trifluoroacetyl chloride (1-3). Trifluoroacetyl chloride is preferred over trifluoroacetic anhydride because of its greater reactivity (33). Use of 4-dimethylaminopyridine as the acylation catalyst was suggested by Dorn, et al. (2). Use of water-soluble derivatization agents throughout enabled clean-up of the crude reaction mixture via aqueous extraction. The inherent hydrophobicity of fluorinated derivatives (35) helps to prevent significant product loss during the extraction.

As discussed above, IR measurement of underivatized hydroxyl bands suffers from interference by water, which is typically present in equal or greater molar concentration than organically bound hydroxyls in many crudes and fuels, and hydrogen bonding effects. The free OH band also exhibits a low molar absorptivity, which makes detection of hydroxyls difficult in virtually all types of crudes except coal liquids, where phenols are typically present at percent levels. Similarly, direct measurements of carboxyls is complicated by interference from other carbonyl types and the presence of both monomeric and dimeric species in solvents typically employed for IR measurements. For these reasons, a derivatization approach such as the one shown above offered significant potential advantages. In addition, hydrogen-bonding effects would be greatly reduced for other bands of interest--e.g., N-H, SO, and other C = O--by the combined esterification-acylation of carboxyls and hydroxyls. Of course, it was essential that chemical moieties added in the reaction yield bands which were both self-resolved and provided minimal overlap with other carbonyl species typically present in fossil fuels.

The objective of the work was to determine the feasibility and practicality of the derivatization approach and compare it with conventional IR analysis of underivatized hydroxyl and carboxyl bands. The inherent simplicity, lower cost, and wide availability of IR compared to NMR and other more sophisticated instrumental techniques was a major factor in its selection. Conventional sample handling methods and a dispersive instrument

were employed. For calibration and verification of the method, whole acid concentrates and subfractions previously isolated from Cerro Negro heavy oil (36), SRC-II coal liquid (37), Wilmington, CA, petroleum (38), and selected commercial refinery streams were employed. The preceding derivatization scheme has also been extensively applied to GC/MS determination of specific hydroxyaromatic compounds in fuels and crudes. That work will be reported separately.

EXPERIMENTAL SECTION

Apparatus

All IR measurements were made with a Perkin-Elmer (Norwalk, CT) model 283 spectrophotometer. Conventional amalgamated KBr liquid cells, nominal 0.5 mm pathlength, were employed. The instrument was set up and operated under "normal" scanning conditions suggested by the manufacturer. With the slit program and scan speeds employed, the instrument manual specified a scan rate of $4.2 \text{ cm}^{-1}/\text{sec}$ and spectral band pass of $2\text{--}2.5 \text{ cm}^{-1}$ for the region from 1800 to 1600 cm^{-1} .

Reagents

All solvents were high purity grade (OmniSolv[®], EM Science, Cherry Hill, NJ). Trifluoroacetyl chloride was obtained from SCM (Gainesville, FL), acetic anhydride (99+%) 2,2,2-trifluoroethanol (99+%), and 4-dimethylaminopyridine (99%) were obtained from Aldrich (Milwaukee, WI). Inorganic reagents were of ACS grade. Organic compounds used for molar absorptivity determinations typically assayed at 97% or better and were obtained from commercial sources.

Procedure

The optimized derivatization procedure was as follows. A known weight of material, typically 5-10 mg, was added to 1 mL of 9:1 (V/V) trifluoroacetic anhydride:2,2,2-trifluoroethanol. Esterification was accomplished by heating this mixture in a 5 mL reaction vial to 60°C for ca. 15 min. The resulting

product was prepared for acylation by addition of 4 mL of a solution of 0.25 M 4-dimethylaminopyridine (DMAP) in dichloromethane. Acylation was carried out by simply bubbling the solution with trifluoroacetyl chloride (TFACl) gas for 30 min at room temperature. A short piece of fused silica tubing, ca. 20 cm (length) x 0.25 μ m (i.d.), proved ideal for delivery of the TFACl. The cylinder was also fitted with a metering valve for flow control. Excess reagents and trifluoroacetic acid produced as a by-product were removed via extraction with 20 mL of aqueous 0.167 M Na_2HPO_4 -0.083 M NaH_2PO_4 buffer. The extraction process was repeated to ensure complete removal, and the resulting dichloromethane solution was dried by passing it through a 4 mL cartridge of anhydrous Na_2SO_4 . Quantitative elution from the cartridge was effected by flushing it with an additional 5-10 mL dichloromethane. The purified product was taken to near dryness under a stream of nitrogen and diluted to a known volume, typically 1 mL, prior to IR measurements. Evaporation of excess dichloromethane yielded a more concentrated solution for improved sensitivity, and removed the relatively volatile 2,2,2-trifluoroethyl trifluoroacetate by-product which interfered in the determination of total hydroxyl content.

Absorbance was measured at band maxima relative to a solvent versus solvent baseline. In each case, repetitive determinations were performed over a series of dilutions of the stock solution to check linearity of absorbance versus concentration. Molar absorptivities were calculated from regression analysis of the linear portion of these plots, in accordance with Beer's law. Typically, significant deviation from linearity was observed whenever absorbance exceeded 0.3 units. Band maxima for trifluoroacetate derivatives occurred near 1800 cm^{-1} ; those for 2,2,2-trifluoroethyl esters ranged from 1760 - 1740 cm^{-1} . Spectra of underivatized compounds and petroleum fractions were also obtained from dichloromethane solutions and were interpreted in an analogous manner.

Concentrations (wt %) of hydroxyl-containing compounds and carboxylic acids in crudes, fuels, or their fractions were calculated from the measured intensities of the appropriate bands per unit weight, corresponding measured or estimated average molecular weights, and average molar absorptivities for the respective bands determined from calibration with pure compounds and

selected petroleum or synfuel fractions. In cases where average molecular weights were inappropriate or could not be determined or reasonably estimated, the concentration of the functional group proper was reported in lieu of the compound type.

Liquid chromatographic procedures for isolating fractions used in calibration and verification of the method have been described previously (38-41). Briefly, whole acid fractions were isolated using nonaqueous ion exchange liquid chromatography (38). Whole acids were subfractionated via normal phase HPLC on silica using a mobile phase containing tetramethylammonium hydroxide (39-41). In cases where acid fractions or subfractions were used to determine average molar absorptivities, their hydroxyaromatic or carboxylic acid content was independently assayed using one or more of the following techniques: elemental analysis, nonaqueous titration with potassium dimsyl (39), IR (without chemical derivatization (39)), and GC/MS (41). The resulting molar absorptivities were corrected for the presence of nonhydroxyl or noncarboxyl types as required. Average molecular weights were estimated by nonaqueous titration and/or vapor pressure osmometry techniques (42).

RESULTS AND DISCUSSION

Optimization of the Derivatization Procedure

Initial efforts focused on maximizing product yields and recoveries, minimizing interferences, and improving practical aspects of the derivatization procedure.

In the case of acylation, obtaining quantitative product yields presented little difficulty, except in cases of severely hindered hydroxyaromatics like 2,6-di-tert-butylphenols--which are essentially nonreactive. Substitution of DMAP as the acylation catalyst significantly decreased reaction time and improved yields of products from partially hindered hydroxyaromatics, such as 2-tert-butyl-6-methylphenol, over those obtained with an earlier procedure utilizing triethylamine (41). An appreciable excess of catalyst is required, since it also acts as a scavenger for HCl produced during acylation (1). In GC/MS analysis of pure hydroxyaromatic compounds or actual samples, detection

of nonacylated species was rare, and their relative concentration very seldom exceeded 1% of the total present.

The corresponding situation for esterification of carboxylic acids may have been similar, but was much more difficult to ascertain. The main difficulty arose from the poor GC characteristics of free carboxylic acids, which made GC/MS detection of unreacted pure carboxylic acids difficult, and virtually impossible in the case of actual petroleum fractions. Since Smith and Tsai (27) reported yields in excess of 98% using 2,2,2-trichloroethanol, initial reaction conditions were identical to their procedure. Systematic variation of reaction conditions and molar ratios of reagents/reactant in order to maximize IR response led to only a slight modification of the Smith and Tsai procedure: a 60° C versus 100° C reaction temperature. The lower temperature was largely employed for practical convenience and because reagent loss from evaporation was less. Reaction time was extended slightly to compensate for the lower temperature.

The major challenge was development of an adequate method for removal of excess reagents and reaction by-products from the crude reaction product. All the reagents except DMAP exhibited sufficient volatility to be easily removed by evaporation. However, a suitable adsorbent for subsequent removal of DMAP and trifluoroacetic acid, a reaction by-product, could not be found. Potassium carbonate, suggested by Sleevi, et al. (1), Li_2CO_3 , LiOH , Ag_2O , Al_2O_3 , CaO , SiO_2 , and several commercial chemically-bonded silica adsorbents were tried. Apparently, interaction between DMAP and trifluoroacetic acid prevented effective removal by any of the adsorbents investigated; significant losses of sample also occurred on several of the above adsorbents. Thus, the aqueous extraction proved to be a much more effective alternative. The pH of the aqueous buffer was optimized through repetitive reactions of selected pure compounds to determine the $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ ratio yielding the highest IR response, i.e. recovery of product, consistent with complete trifluoroacetic acid removal. A citric acid buffer system was also evaluated. Although aqueous extraction has the potential disadvantage of promoting hydrolysis of reaction products, especially trifluoroacetate esters (8), this possibility

was minimized by pH optimization, performing the extractions rapidly, and subsequent drying over sodium sulfate. Trifluoroacetic acid exhibits carbonyl absorption in the same region of the IR as trifluoroacetate esters, thereby necessitating its quantitative removal.

Direct acylation of petroleum fractions, or other sample types containing carboxylic acids, proved infeasible owing in part to formation of mixed anhydrides which interfered with the IR determination of trifluoroacetate esters. Mixed anhydride formation during reaction of trifluoroacetic anhydride with a variety of carboxylic acids is well documented (31). This apparently also occurs during direct acylation with TFACl. In addition, GC/MS analysis of *o*-toluic acid which had been exposed to TFACl revealed significant amounts of the corresponding acid chloride. Furthermore, many of these interfering species are stable to hydrolysis during the aqueous extraction. Thus, the initial esterification of carboxylic acids with 2,2,2-trifluoroethanol is required to prevent subsequent formation of anhydrides/acid chlorides in the acylation step which interfere in the determination of hydroxyl compounds as their trifluoroacetates. Unless a given fraction is certifiably free of carboxylic acids, it is recommended that the complete reaction sequence be performed, even though only the hydroxyl compounds may be of interest.

In much of the prior work, TFACl (b.p. -18°C) acylations have been carried out at dry ice/solvent temperatures (1-3,40), nominally to increase the effective concentration of TFACl in the reaction medium. Practical experience has shown this precaution to be unnecessary, however, with acceptable reaction rates achieved by simply saturating dichloromethane with TFACl at room temperature. Also, in the course of this work and during subsequent application of the method, cylinders of TFACl have occasionally been received which, through atmospheric contamination or similar means of water introduction, are highly contaminated with HCl gas. This problem is immediately recognizable by the subsequent precipitation of the DMAP catalyst by HCl within a short time. Mediocre product yields are typically obtained

with contaminated TFACl, and those cylinders should be returned or discarded. Furthermore, the TFACl delivery apparatus should be stoppered while not in use, by impinging a GC septum onto the tip of the fused silica tubing, to prevent entry of atmospheric moisture.

General Characteristics of Spectra Before and After Derivatization

Figure 1 shows portions of the IR spectrum of phenol and benzoic acid where OH and carbonyl stretching bands occur. Because neither compound was dried prior to obtaining its spectrum, both show water-derived contributions to OH stretching (3690 , 3610 cm^{-1}) and bending (1610 cm^{-1}) bands. Aromatic C=C vibrations also contribute to the band observed near 1600 cm^{-1} . Since the free carboxyl OH band occurs at a lower wavenumber (3520 cm^{-1}) than the OH band of phenol (3590 cm^{-1}), both water-derived OH stretching bands are apparent in the benzoic acid spectrum, while the phenolic OH band overlaps the lower wavenumber water band in its spectrum. In quantitative IR determination of phenolic/alcoholic hydroxyls, the intensity of the combined OH band at ca. 3600 cm^{-1} is corrected for water contribution by subtracting 41% of the absorbance of the resolved H_2O band (3690 cm^{-1}). The approximate 2.5:1 ratio of the $3690\text{ cm}^{-1}/3600\text{ cm}^{-1}$ H_2O band intensities is evident in the benzoic acid spectrum. Carbonyl bands representing monomeric versus hydrogen bonded benzoic acid dimers are clearly resolved. Corresponding carbonyl absorption patterns for saturated carboxylic acids are similar, except the wavenumber of each band is typically 15 cm^{-1} higher.

Figure 2 shows portions of IR spectra containing carbonyl bands from the corresponding derivatives of phenol and benzoic acid, as well as derivatized 4-hydroxybenzoic acid. The only OH bands evident in any of those spectra were from small amounts of water carried over from the aqueous extraction. The carbonyl bands from trifluoroacetate and 2,2,2-trifluoroethyl esters are easily resolved and, in the case of the compounds shown, of nearly equal intensity. The small doublet at ca. 1800 cm^{-1} in the spectrum of 2,2,2-trifluoroethyl benzoate (Fig. 2B), is characteristic of trifluoroacetic acid (monomer- 1810 cm^{-1} , dimer- 1790 cm^{-1}), which was incompletely removed in that case.

FIGURE 1. - IR spectra of phenol and benzoic acid. Concentrations are 5.58 and 1.45 mg/mL CH_2Cl_2 , respectively. Dashed line is solvent versus solvent baseline.

FIGURE 2. - Partial IR spectra showing carbonyl absorption from derivatized phenol (A), benzoic acid (B), a 1:1 mixture of phenol and benzoic acid (C), and 4-hydroxybenzoic acid (D). Concentrations of A-D are 1.20, 1.50, 0.90/1.07, and 1.77 mg/mL CH₂Cl₂, respectively.

Figure 3 compares spectra of a whole acid fraction from a high boiling petroleum distillate before (A) and after (B) derivatization. The following features are apparent in the spectrum of the underivatized acids: 1) the weak intensity of the OH band at 3600 cm^{-1} , which is typical for petroleum fractions, 2) the significant contribution by water to the 3600 cm^{-1} band indicated by intensity of the 3690 cm^{-1} band, due to water alone, and the assumption of a 2.5:1 intensity ratio for $3690/3610\text{ cm}^{-1}$ bands from water, 3) significant overlap between the OH band from carboxyl groups (3500 cm^{-1}) and the N-H stretching band from pyrrolic benzologs present, 4) distinct bands for carboxylic acid monomers and dimers, and 5) the presence of other carbonyl types indicated by broad absorption near 1650 cm^{-1} . In contrast, only the N-H band is observed in the upper region of the derivatized acid spectrum. In addition, well resolved carbonyl bands representing absorption by trifluoroacetate and 2,2,2-trifluoroethyl esters are observed, along with an unidentified carbonyl band at 1660 cm^{-1} which may represent amides analogous to 2-quinolone. The wavenumber (1760 cm^{-1}) of the 2,2,2-trifluoroethyl esters is typical of aliphatic carboxylic acids; aromatic acids, i.e. where the carboxyl group is directly substituted onto the aromatic ring, typically absorb near 1740 cm^{-1} (see Figure 2). Due to their predominantly aliphatic nature (44), a single band at ca. 1760 cm^{-1} is normally observed for petroleum carboxylic acids.

Table 1 summarizes wavenumbers corresponding to band maxima ($\tilde{\nu}_{\text{max}}$) and average molar absorptivities (ϵ) at $\tilde{\nu}_{\text{max}}$ for plain and derivatized hydroxyl and carboxyl groups. Determination of these parameters is discussed in detail in the next section. The range given for $\tilde{\nu}_{\text{max}}$ represents that normally encountered in spectra of petroleum, synfuels, and representative pure components. The variation of ϵ with structure, approximated in the table by the standard deviation of ϵ 's for individual compounds, was approximately $\pm 10\%$ relative for each band measured, regardless of type. Good agreement between ϵ for derivatized pure phenols (610 ± 50) and petroleum hydroxyls (600 ± 40) was obtained. However, petroleum carboxyls yielded lower ϵ 's than any of the pure compounds investigated. As noted previously, trifluoroacetate esters of hydroxyl groups exhibit a much greater IR response ((5-7:1) than plain OH groups. At first glance, the corresponding situation for 2,2,2-trifluoroethyl esters versus plain carboxyls appears reversed, with an average decrease in ϵ of nearly 50% after esterification. However, since carboxyls give rise to two bands and esters only one, their practical IR sensitivities are about equal.

FIGURE 3. - IR spectra of underivatized (A) and derivatized (B) Cerro Negro 550-700° C acids. Concentrations are 14.0 (A) and 19.1 (B) mg/mL CH_2Cl_2 . See text.

TABLE 1. - Band maxima ($\tilde{\nu}_{\max}$) and molar absorptivities (ϵ) of IR bands corresponding to underivatized and derivatized OH and C(O)OH groups¹

Functional Group	Underivatized		Derivatized	
	$\tilde{\nu}_{\max}$ (cm ⁻¹) ²	ϵ (Lm ⁻¹ cm ⁻¹) ³	$\tilde{\nu}_{\max}$ (cm ⁻¹)	ϵ (Lm ⁻¹ cm ⁻¹)
A. From Pure Compounds				
OH (alcoholic)	3610 $\pm$ 10	60 $\pm$ 10	1785 $\pm$ 5	420 $\pm$ 40
OH (phenolic)	3590 $\pm$ 10	120 $\pm$ 10	1800 $\pm$ 5	610 $\pm$ 50
C(O)OH (aliphatic)	1750 $\pm$ 5 (monomer) } 1715 $\pm$ 5 (dimer)	580 $\pm$ 40	1755 $\pm$ 5	330 $\pm$ 20
C(O)OH (aromatic)	1740 $\pm$ 10 (monomer) } 1700 $\pm$ 10 (dimer)	610 $\pm$ 40 ⁴	1740 $\pm$ 5	370 $\pm$ 30 ⁴
B. From Petroleum Fractions				
OH	3600 $\pm$ 10	nd	1800 $\pm$ 5	600 $\pm$ 40
C(O)OH	1750 $\pm$ 5 (monomer) } 1710 $\pm$ 5 (dimer)	470 $\pm$ 40	1760 $\pm$ 5	280 $\pm$ 14

¹For dilute dichloromethane solutions, ca. 1-10 mg/mL.

²Median $\pm$ range for petroleum and related pure compounds.

³Mean $\pm$ 50.

⁴Results for *p*-alkyl and 2-naphthoic acids were excluded from the mean. ϵ 's for *p*-alkyl and 2-naphthoic acids were approximately 50% greater than those of other aromatic acids.

Significance and Variability of ϵ

Tables 2 and 3 list $\tilde{\nu}_{\max}$ and ϵ for individual hydroxyl and carboxyl compounds, respectively. These data were used to determine average parameters shown earlier in Table 1. In general, the results obtained for ϵ at $\tilde{\nu}_{\max}$ or other wavenumbers are highly dependent on instrumental parameters--especially effective slit width, grating or interferometer performance, and other factors affecting the monochromatic quality of the IR radiation (45). Thus, the present data agree well with prior data in some cases (e.g., ethyl acetate: ϵ = 393 (this work), ϵ = 358 (46); octadecanoic acid: ϵ = 606 (this work), ϵ = 564 (46)) and disagree significantly in others (e.g., ethyl *n*-butyrate: ϵ = 376 (this work), ϵ = 600 (47)). Hence, although the present data are internally consistent, they are not universally applicable. Integrated absorption intensities are less dependent on instrumental factors (48). They were not routinely employed in this work in part because of the lack of a convenient means for integrating absorption bands with the instrumentation

TABLE 2. Band maxima ($\tilde{\nu}_{\max}$) and molar absorptivities (ϵ) of underivatized and derivatized hydroxyl compounds

Compound	Underivatized		Derivatized	
	$\tilde{\nu}_{\max}(\text{cm}^{-1})$	$\epsilon(\text{Lm}^{-1}\text{cm}^{-1})$	$\tilde{\nu}_{\max}(\text{cm}^{-1})$	$\epsilon(\text{Lm}^{-1}\text{cm}^{-1})$
I. Alcohols				
water	3690	44	NA ¹	
	3610	18		
ethanol	3620	43	1790	460
1-dodecanol	3620	60	1790	437
1-indanol	3600	55	1780	368
2-indanol	3610	57	1780	395
9-fluoreno1	3620	70	1790	546
$\bar{X} \pm \text{SD}$		58±9		415±41 ³
II. Hydroxyaromatics				
phenol	nd ²	-	1800	622
2-methylphenol	3600	93	1800	690
3-methylphenol	3600	121	1800	609
4-methylphenol	3600	116	1800	485
2,6-dimethylphenol	3600	103	1800	679
2,5-dimethylphenol	3600	102	1800	581
3,5-dimethylphenol	nd	-	1800	615
2-ethylphenol	nd	-	1800	574
3-ethylphenol	nd	-	1800	569
4-ethylphenol	nd	-	1800	534
3,4,5-trimethylphenol	3600	123	1800	634
2-isopropylphenol	nd	-	1800	664
3-isopropylphenol	nd	-	1800	659
4-isopropylphenol	nd	-	1800	605
2-n-propylphenol	nd	-	1800	602
4-n-hexylphenol	nd	-	1800	586
5-indanol	3600	128	1800	562
1-naphthol	3600	121	1800	583
2-naphthol	3580	146	1800	556
2-methyl-1-naphthol	nd	-	1800	631
2-phenylphenol	3600	121	1800	692
4-phenylphenol	3600	126	1800	560
4-benzylphenol	3600	108	1800	669
$\bar{X} \pm \text{SD}$		117±14		607±53
III. Dihydroxyaromatics⁴				
1,3-dihydroxybenzene	nd	-	1810	466
2,2'-dihydroxybiphenyl	nd	-	1800	511
4,4'-dihydroxybiphenyl	nd	-	1800	664
IV. Thiophenols				
2-methylthiophenol	nd	-	1720	348

¹Not applicable.

³Result for 9-fluoreno1 excluded from mean.

²Not determined.

⁴Results reported on a per hydroxyl group basis.

TABLE 3 - Band maxima ($\tilde{\nu}_{\max}$) and molar absorptivities (ϵ) of underivatized and derivatized carboxylic acids

Compound	Underivatized			Derivatized	
	$\tilde{\nu}_{\max}$ (cm ⁻¹) monomer	$\tilde{\nu}_{\max}$ (cm ⁻¹) dimer	ϵ (Lm ⁻¹ cm ⁻¹) ¹	$\tilde{\nu}_{\max}$ (cm ⁻¹)	ϵ (Lm ⁻¹ cm ⁻¹)
I. Aliphatic Acids					
trifluoroacetic	1810	1790	445	nd ²	-
decanoic	1750	1710	589	1760	328
undecanoic	1750	1715	532	1760	346
octadecanoic	1750	1720	606	1760	362
eicosanoic	1755	1715	624	1760	318
cyclopentanecarboxylic	1750	1710	586	1755	306
cyclohexanecarboxylic	1750	1710	625	1750	323
3-cyclohexylpropanoic	1750	1720	580	1760	348
phenylacetic	1750	1720	524	1760	326
5-phenylpentanoic	nd	-	-	1760	333
1-naphthylacetic	nd	-	-	1760	330
$\bar{X} \pm SD$			583 $\pm$ 38 ³		332 $\pm$ 16
II. Aromatic Acids					
2-methylbenzoic	1740	1700	655	1740	363
2,3-dimethylbenzoic	1750	1695	599	1740	351
2-phenylbenzoic	1745	1705	573	1750	365
1-naphthoic	1735	1700	632	1735	346
1-fluorenenecarboxylic	nd	-	-	1740	395
9-anthracenecarboxylic	nd	-	-	-	420
$\bar{X} \pm SD$			615 $\pm$ 36		373 $\pm$ 29
4-methylbenzoic	1730	1695	919	1740	535
4-n-heptylbenzoic	1735	1700	986	1740	579
2-naphthoic	1740	1700	933		532
$\bar{X} \pm SD$			946 $\pm$ 35		549 $\pm$ 26
III. Ethyl esters					
ethyl acetate	1740	-	393		
ethyl n-butyrate	1730	-	376		
diethyl					
2,4-dimethylglutarate	1730	-	395 ⁴		
$\bar{X} \pm SD$			388 $\pm$ 10		

¹Combined ϵ for monomer + dimer.

²Not determined.

³Result for trifluoroacetic acid excluded from mean.

⁴ ϵ on a per ester group basis.

available. In addition, rather marginal improvement in data precision was obtained in cases where manual band integration was performed owing to the uniform band width typically observed for both trifluoroacetate and 2,2,2-trifluoroethyl esters. In the case of free hydroxyls, however, band integration probably would have increased the uniformity of apparent IR response. Finally, because of the dependence of IR response on other factors such as cell characteristics, detector performance and operator technique, at least a limited recalibration would be necessary for application of the present work in another laboratory, regardless of efforts taken to obtain "ultimate" intensity data.

Inspection of Tables 2 and 3 led to the empirical correlations of carbonyl intensities with structure shown in Table 4. Although it is known that the magnitude of ϵ depends on the dipole change produced by a given vibration, correlating this effect with structure presents a considerable challenge. It is interesting to note that in the case of esters, a given substituent or structural modification generally exhibited opposite effects at the carbonyl carbon versus the single bonded oxygen positions. For example, the effects of α versus β -naphthyl substitution, and increasing aromaticity of substituted arene groups are noted in the table. Also, *p*-alkylation dramatically increased ϵ over that of *o*- and *m*-substituted 2,2,2-trifluoroethyl alkylbenzoates. However, in the case of phenyl trifluoroacetates, *p*-alkylation usually decreased ϵ compared to *m*- and especially *o*-alkyl isomers.

The lower ϵ of trifluoroacetic acid versus nonhalogenated alkanolic acids corresponds to a similar decrease noted for brominated ketones (48). The decrease in response for 2,2,2-trifluoroethyl compared to ethyl esters is significantly less than observed from halogenation at α -carbons; the relative magnitude observed for α versus β halogenation on ϵ corresponds to that typically observed for primary versus secondary inductive effects. The higher response of aromatic versus aliphatic acid esters corresponds to that observed for alkylaryl versus dialkyl ketones (46). Similarly, the greater carbonyl intensity of carboxylic acids compared to esters has also been noted (46). The dependence of ϵ on detailed structural effects such as alkyl chain length and degree of branching was not investigated in detail here or in the literature, but the available data suggest a complex relationship. Since the repeatability of ϵ ranged from 2-5% (RSD), the differences in ϵ 's of structurally related compounds were usually not considered significant unless they exceeded 10%.

TABLE 4. - Summary of structural effects on carbonyl intensities

Basic Structure	Variation	Effect on ϵ
RCOH	replace H with CH_2CH_3	~ 30% decrease
	replace H with CH_2CF_3	~ 40% decrease
	replace R with Arene	NC ¹ (non-p-substituted) ~ 50% increase (p-substituted)
	replace R with CF_3	~ 25% decrease
F_3CCOH	replace H with alkyl group	NC ¹
	replace H with Arene	~ 40% increase
$\text{F}_3\text{CCO}-\text{C}_6\text{H}_4\text{R}$	increase alkyl chain length	o-substituted ($\text{CH}_3 > \text{iso-C}_3\text{H}_7 > \text{n-C}_3\text{H}_7 > \text{C}_2\text{H}_5$) m-substituted ($\text{iso-C}_3\text{H}_7 > \text{CH}_3 > \text{C}_2\text{H}_5$) p-substituted ($\text{iso-C}_3\text{H}_7 > \text{n-C}_6\text{H}_{13} > \text{C}_2\text{H}_5 > \text{CH}_3$)
$\text{1-naphthyl-COCH}_2\text{CF}_3$	substitution at 1 vs 2 naphthyl position	$2 > 1$
$\text{F}_3\text{CCO}-\text{1-naphthyl}$	substitution at 1 vs 2 naphthyl position	$1 \geq 2$
$\text{ArCOCH}_2\text{CF}_3$	increase aromaticity of Ar	$\text{anthracene} > \text{fluorene} > \text{naphthalene} \approx \text{benzene}$
F_3CCOAr	increase aromaticity of Ar	$\text{benzene} > \text{naphthalene}$

¹NC = no change

Variations in instrument performance and IR transmission quality of sample cells limited the long term repeatability of ϵ and of IR measurements in general. Other variables such as solvent quality may also have impacted repeatability. Variation in product yield and recovery did not generally control precision in the determination of ϵ for derivatives. For example, repetitive determination of ϵ for commercially prepared (Pfaltz and Bauer, Waterbury, CT) phenyl trifluoroacetate (97%) over a two-year period yielded the following results: 627, 614, 622, 626, and 689 $\text{Lm}^{-1}\text{cm}^{-1}$, $\bar{x} = 636$; $\text{SD} = 30$, $\text{RSD} = 4.7\%$. Corresponding data for derivatives yielded representative RSD's of 4.2% (decanoic acid), 1.8% (2-phenylbenzoic acid), 3.1% (2-naphthol), and 5.5% (phenylacetic acid). Although rejection of the 689 result for phenyl trifluoroacetate improves its RSD to 1.0%, analogous treatment of data for derivatives improves their RSD's as well. Overall, data fluctuation correlated better with chronology and cell use patterns than with whether or not derivatization was employed prior to determination of ϵ .

Although preceding results indicate that the compound to compound variation in ϵ from structural effects is only 2-3 times the RSD for individual ϵ 's, further investigation of ϵ on actual petroleum fractions was warranted for the following reasons: 1) only a limited set of ϵ data were available for each compound type, 2) within a given type, selection of individual compounds was based more on availability than on anticipated concentration in petroleum, 3) at least in the case of carboxylic acids, structures of the available pure compounds differed significantly from those previously identified in petroleum, and 4) additivity of ϵ 's and other phenomena potentially affecting results obtained on gross mixtures versus single compounds had not been investigated. Furthermore, inherent structural differences in various types of crudes (49) could cause systematic variations in ϵ with crude type. The limiting factors in the determination of ϵ on actual petroleums were 1) isolation of fractions of sufficient purity and 2) obtaining reliable assays for either hydroxyl or carboxyl content in those fractions.

Tables 5 and 6 show results obtained on hydroxyaromatic (ArOH) and carboxylic acid concentrates, respectively. In general, ϵ 's for hydroxyaromatic concentrates compare favorably with the average for pure compounds, while those for carboxylic acids are significantly lower. Precision of ϵ data was comparable to that of pure compounds in cases where multiple determinations were made.

TABLE 5. - Band maxima ($\tilde{\nu}_{\max}$) and molar absorptivities (ϵ) of underivatized and derivatized hydroxyaromatic concentrates from fuels

Fuel	Boiling Range (°C)	Underivatized		Derivatized	
		$\tilde{\nu}_{\max}$ (cm ⁻¹)	ϵ (Lm ⁻¹ cm ⁻¹)	$\tilde{\nu}_{\max}$ (cm ⁻¹)	ϵ (Lm ⁻¹ cm ⁻¹)
Raw SRC-III ¹	200-325	3600	110	1800	539±30
Coal Liquid					
Hydrotreated ^{1,2}	200-325	3600	118	1800	623±11
SRC-II					
Petroleum-derived JP-5					
(as received)	170-280	nd ⁵	-	1800	631
(thermally stressed) ³		nd	-	1800	608
LCO ⁴	200-325	3600	71	1800	576
LCO ⁴					
	150-325	3600	59	1800	610
$\bar{X} \pm SD$			nd		598 ± 34

¹For sample documentation see (37) and Sutterfield, D.; Lanning, W. C.; Royer, R. E. Upgrading Coal Liquids; Sullivan, R. F., Ed.; Adv. Chem. Ser. No. 156, Am. Chem. Soc.: Wash, DC, 1981; chapter 5.

²NiMo catalyst, 310°C, 0.5 LHSV, 980 SCF H₂/bbl.

³JFTOT thermal stability test, ASTM D 3241.

⁴Light cycle oil from commercial scale catalytic cracking unit.

⁵Not determined.

TABLE 6 - Band maxima ($\tilde{\nu}_{\max}$) and molar absorptivities (ϵ) of underivatized and derivatized carboxylic acid concentrates from virgin petroleum distillates

Crude	Distillate Boiling Range (°C)	Underivatized			Derivatized	
		$\tilde{\nu}_{\max}$ (cm ⁻¹) monomer	$\tilde{\nu}_{\max}$ (cm ⁻¹) dimer	ϵ (Lm ⁻¹ cm ⁻¹) ¹	$\tilde{\nu}_{\max}$ (cm ⁻¹)	ϵ (Lm ⁻¹ cm ⁻¹)
Cerro Negro ²	200-425	1750	1715	476	1755	266
	425-550 ³	1745	1710	479	1755	266
		1750	1710	468	1755	279
	550-700	1745	1710	407	1760	159
Wilmington ⁴	225-370	1750	1715	643	1760	298
	370-535	1750	1710	514	1760	290
$\bar{X} \pm SD^5$				469 ± 39		280 ± 14

¹Combined ϵ for monomer + dimer.

²For sample documentation, see (36,42).

³Separations were performed in duplicate. Results shown are for respective fractions.

⁴For sample documentation, see (22,38).

⁵Wilmington 225-370° C (underivatized) and Cerro Negro 550-700° C (derivatized) results were excluded from their respective means.

The ArOH concentrates employed for determination of ϵ were also analyzed in detail by GC/MS. Correlation of ϵ 's in Table 5 with composition yielded some interesting results. For example, *m*- and *p*-alkyl-phenols predominated in the raw SRC-II coal liquid fraction, whereas *o*-alkylphenols were much more enriched in the hydrotreated SRC. The relative abundance of other ArOH paralleled that of the phenols, e.g., the ratio of 4-indanol to 5-indanol was <0.5 before and 4.7 after hydrotreating. Thus, the higher result for ϵ in the case of the derivatized hydrotreated SRC fraction is consistent with the generally higher ϵ 's of pure *o*-alkylphenol derivatives (Table 2), and the result for the raw SRC was comparable to that of compounds present in high abundance such as 3-ethylphenol, 4-ethylphenol, and 5-indanol (Table 2). The petroleum-derived JP-5 fraction exhibited a much higher degree of alkylation than either SRC fraction, with easily detectable levels of alkylphenols containing up to 11 carbons in alkyl groups. Its relatively high ϵ value is consistent with the probability of a substantial percentage of *o*-substituted compounds, given the degree of alkylation observed. Also, the main structural change observed after thermal stressing was a net lowering in the degree of alkylation, which is consistent with the lower ϵ obtained on the ArOH fraction from the stressed fuel. Although petroleum derived, the distribution of ArOH in light cycle oils (LCO) is quite different from that of virgin petroleum distillates. Significant proportions of plain and alkylated polynuclear species such as naphthols and fluorenols are present in addition to phenols and hydroxybiphenyls. Nevertheless, molar absorptivities for the two derivatized LCO concentrates examined were comparable to those of the other fuels. The LCO fraction yielding the smaller value of ϵ (576) contained a higher proportion of polynuclear ArOH; the trend of lower ϵ 's for those types relative to phenols was noted earlier in Table 4.

The exceptionally low ϵ 's obtained for underivatized LCO ArOH concentrates probably resulted from hydrogen bonding interactions with nitrogen compounds present as contaminants. Although ϵ 's for both underivatized and derivatized fractions were corrected for their dilution effect, the nitrogen compounds apparently effected a net lowering in the ϵ observed for free hydroxyls beyond that accountable for by simple dilution. This effect appeared to be negligible after derivatization. Conversely, ϵ 's consistent with pure ArOH were obtained for both underivatized SRC fractions, which were relatively free of other types.

ϵ 's obtained for both underivatized and derivatized petroleum carboxylic acid concentrates (Table 6) were generally lower than those of pure saturated carboxylic acids (Table 3). Since repeated attempts at assaying these fractions indicated essentially 100% carboxylic acid content in all cases, this lower response in all boiling ranges has tentatively been attributed to structural effects. Carboxylic acids from Wilmington and other California crudes have been studied extensively by Seifert and coworkers (50), and others (44); they are predominantly based on polycyclic alkane structures. Corresponding data are not available for Cerro Negro acids. In all probability, the pure compounds used to determine ϵ for aliphatic acids inadequately represent either petroleum both in terms of structure and IR response.

Considering their complex and variable composition, the agreement obtained between ϵ 's for the various fractions and, in the case of ArOH, their correspondence to data for pure compounds, was surprisingly good. Although the variability of ϵ with composition could be rationalized in the case of ArOH concentrates, this is not generally possible in routine IR applications where measurements are typically performed on whole fuels of essentially unknown composition. In those cases, nominal values of ϵ , e.g., 600 for ArOH and 280 for carboxylic acid derivatives, must be assumed and the corresponding limits on accuracy of the results, ca. $\pm 10\%$ relative, recognized.

Interferences

The probability of interference from other carbonyl species present in petroleum and syncrudes is low, since types normally encountered, e.g., ketones and amides, normally exhibit minimal absorption in the IR regions corresponding to the derivatives. Interference from acylation of types other than ArOH, the most probable source of error, was investigated.

Table 7 lists results from attempted derivatization of selected nitrogen- and oxygen-containing compounds. Pyrrolic benzologs react to varying degrees to yield N-acyl derivatives (ca. 1720 cm^{-1}); in the case of indole, a minor aromatic ring-acylated product was also observed. The carbonyl band from trifluoroacetamides typically poses negligible interference toward the determination of carboxyls; the ring-acylated product from indole directly interferes with hydroxyl determinations to the extent of its formation (16

mole %). Acylation of benzamide resulted in 100% conversion to its mono-trifluoroacetamide, with one carbonyl band directly overlapping that of hydroxyl derivatives (1800 cm^{-1}) and the other (1740 cm^{-1}) contributing to a lesser extent to carboxyl absorption (1760 cm^{-1}). Fortunately, benzamide and other diprotic amides are absent or at least uncommon to petroleum. Mono-protic amides, represented by 4-methyl-2-quinolone, were unreactive. Anilines react to give a mixture of mono- and diacyl-products. For example, 2-methylaniline yielded 70% of the diacyl derivative with the current derivatization procedure. Because of their relatively low $\tilde{\nu}_{\text{max}}$, acylated aniline derivatives also present little interference with the determination of carboxyls.

TABLE 7 - Reactivity and degree of interference from representative nitrogen compounds and ketones

Compound	% Reacted	Product(s) $\tilde{\nu}_{\text{max}}$ (cm^{-1})	Degree of Interference (mole %)
indole	78	1800 1740	16 <<62
1,2,3,4-tetrahydrocarbazole	100	1720	0
carbazole	63	1720	0
benzamide	100	1800 1740	100 <<100
4-methyl-2-quinolone	0	-	-
p-ethylaniline	>100	1730	~0
4-methyl-1-tetralone	10	1800	10
1-indanone	75	1800	75

Reactivity of ketones correlated with the acidity of their corresponding enol forms. Aliphatic ketones were unreactive, but cyclic/benzylic types such as 1-indanone and 1-tetralone formed significant amounts of enolic trifluoroacetates. By comparison, independent studies of keto-enolate equilibria indicated the acidity of 2-indanone ($\text{pka } 12.21$) to be $10^{0.7}$ greater than 2-tetralone, 10^3 greater than benzyl methyl ketone and 10^7 greater than acetone and other simple aliphatic ketones (51,52). Thus, the tendency of indanones, tetralones, and analogous ketones to behave like ArOH in the current procedure arises from their comparable acidities.

As noted in Table 2, thiophenol trifluoroacetates exhibit $\tilde{\nu}_{\max}$'s in the same region as the bulk of the trifluoroacetamides, ca. 1720 cm^{-1} . No aliphatic thiols were investigated, but based on the correspondence between $\tilde{\nu}_{\max}$ of alcohols versus phenols, their trifluoroacetates should exhibit $\tilde{\nu}_{\max}$ in the region from $1720\text{--}1700\text{ cm}^{-1}$. Most petroleum fractions exhibit a band at 1720 cm^{-1} after derivatization which, based on a corresponding decrease in the intensity of the free N-H band at 3460 cm^{-1} , probably represents trifluoroacetamides from pyrrolic benzologs. Current research is aimed at improving the yield from acylation of that type so as to extend the current approach to their estimation as well. Although thiols would theoretically interfere, their concentration relative to N-H types is negligible in most petroleum.

In general, the compound by compound approach for studying interferences was less than satisfactory because of the real possibility of overlooking significant interference from unknown or unanticipated types, the limited availability of pure compounds representative of those in petroleum, and the likelihood of overestimating the importance of known interferences such as those from cyclic ketones. For these reasons, a more global approach involving comparison of results from whole fuels versus those from acidic fractions was adopted. In that case, significant interference from basic or neutral components would lead to much higher results obtained on the whole sample compared to those obtained on the acid fraction proper. Those data are described in the next section in conjunction with other data obtained to demonstrate the general applicability of the method.

Applications, Sensitivity, Accuracy

Table 8 compares results obtained from analysis of acid fractions to those from analysis of whole distillates. In the case of kerosines, jet fuels, most diesel fuels, and other products containing low levels of acidic compounds, 0.5 g of the fuel was diluted approximately 1:1 with dichloromethane and carried through the derivatization procedure. Absorbance of the derivatized fuel was measured against a reference containing an equivalent concentration of fuel in dichloromethane. Use of an equivalent fuel/solvent mixture in the reference cell prevented baseline shifting from low intensity bands such as those from aromatic substitution, etc.

TABLE 8. - Comparison of results obtained on derivatized acid fractions versus whole fuels or distillates¹

Fuel/Distillate	Boiling Range (°C)	Total Acids (wt %) ²	Hydroxyl Compounds (wt %)		Carboxylic Acids (wt %)	
			From Acids ³	From Whole Fuel	From acids ³	From Whole Fuel
Hydrotreated SRC-II coal liquid	200-325	12.8	11.2	11.4	ND ⁴	ND
JP-5	175-240	0.11	0.04	0.07	ND	ND
#2-Diesel (straight-run)	200-350	0.47	0.31	0.19	0.17	0.15
#2-Diesel (straight-run)	250-350	0.45	0.15	0.17	0.18	0.15
LCO	225-350	1.30	0.19	0.14	ND	ND
Gas oil from Wilmington crude	370-535	10.4	1.69	1.64	2.9	2.7

¹Nominal values of 600 (OH) and 280 (RCOOH) were assumed for ϵ in the calculation of wt %.

²Gravimetric yield from nonaqueous ion exchange LC separation.

³Results from analysis of acid fractions are expressed on a whole distillate basis.

⁴ND - none detected.

The results from analysis of the whole fuels were generally equivalent to those obtained from acid fractions, thereby indicating the lack of interference from neutral or basic fuel components. Interestingly, several of the whole petroleum distillates exhibited an additional band at 1780 cm^{-1} . Of the pure compounds investigated, only trifluoroacetates of 1- and 2-indanol exhibited bands in this IR region. This band was approximately 50% resolved from the main trifluoroacetate band at 1800 cm^{-1} and apparently caused minimal interference in the determination of ArOH. The origin of the 1780 cm^{-1} band is currently being investigated; it definitely arises from neutral rather than basic components. Since results for total OH in acid fractions were typically equal to or greater than those obtained on whole distillates, the 1800 cm^{-1} band must represent predominantly ArOH rather than alcohols, which normally partition into the neutral fractions. On the other hand, the occurrence of the 1780 cm^{-1} band in the whole distillate spectrum, coupled with its virtual absence in that of the acid fraction, is consistent with an alcoholic structure.

The sensitivity of the method cannot be rigorously established, since it depends significantly on individual sample characteristics. However, the result obtained for OH compounds in the JP-5 fuel in Table 8 was used to estimate an approximate detection limit. Based on the signal-to-noise (S/N) ratio obtained in that case, a detection limit ($S/N = 2$) of 0.007 wt % hydroxyl compounds in the neat fuel, or 0.0005 wt % O as OH, was calculated. This relatively low limit of detection achievable, relative to most IR determinations, results from the narrow band width and high molar absorptivity of the trifluoroacetate carbonyl absorption. The corresponding limit for 2,2,2-trifluoroethyl esters is 5-10 times higher, owing to their lower ϵ 's, greater band width, and the typically higher level of baseline fluctuation present in their spectral region.

Accuracy is limited by structural dependence of ϵ , as discussed previously. Nevertheless, it was felt that some independent corroboration of the IR-chemical derivatization method was needed to assess any systematic bias in results aside from uncertainties in ϵ . Table 9 compares hydroxyl (effectively ArOH) and carboxyl content of selected petroleum acid fractions for which ϵ 's of individual carboxyl concentrates had been previously determined (Table 6). Thus, although nominal ϵ 's were employed in the calculation of ArOH, fraction-specific ϵ 's were employed for carboxyl determinations for both underivatized and derivatized fractions. Those results are compared against gravimetric yields from HPLC isolation of carboxylic acids and nonaqueous titration results for carboxylic acid content.

On the positive side, no systematic bias in carboxyl content was observed for the IR-chemical derivatization method, or any of the others for that matter. However, the results largely reveal the inexact nature of compound type analysis of petroleum in general. IR analysis without derivatization suffers positive interference from other carbonyl types, which may explain the somewhat higher results obtained without, compared to those obtained with derivatization. HPLC data are affected by errors in fraction handling and incomplete separation. These factors can result in either high or low results, in agreement with the random variation observed for those data. Errors in nonaqueous titration are largely positive, either from co-titration of noncarboxylic species or from incomplete neutralization of weaker acids. The latter effect causes results for carboxylic acids to be high, since carboxylic acid content is computed from the ratio of the first equivalence point (assumed to be carboxylic acids) to the total neutralization factor. Without a petroleum with certified carboxylic content, a more precise assessment of accuracy is not possible.

On the other hand, the agreement between hydroxyl content determined with and without derivatization was surprisingly good, considering that nominal values of ϵ were employed in each case. An independent method for assessing hydroxyl content was not available; several published NMR methods for determining ArOH are currently undergoing evaluation in the authors' laboratory for their applicability to petroleum.

TABLE 9. - Comparison of IR results on petroleum acid fractions with those from other techniques

Crude ¹	Distillate Boiling Range (°C)	Wt % of Acid Fraction					
		Hydroxyl Compounds		Carboxylic Acids		HPLC ⁵	NAT ⁶
		IR (w/o Der.) ²	IR (w/Der.) ³	IR (wo/Der.) ⁴	IR (w/Der.) ⁴		
Cerro Negro	200-425	9.7	10.0	64±2 ⁷	55	63±2	57
	425-550	6.7	6.8±0.1	58±2	51±1	56±1	56±1
	550-700	5.4	6.5	47	41	36	42±2
Wilmington	225-370	nd ⁸	24	56	46	46	61
	370-535 ⁹	nd	26	57	54	47	55±1

¹Same crudes as in Table VI.

²Results based on $\epsilon = 120 \text{ Lm}^{-1} \text{ cm}^{-1}$.

³Results based on $\epsilon = 600 \text{ Lm}^{-1} \text{ cm}^{-1}$.

⁴Individual ϵ 's in Table VI were used to calculate wt %.

⁵Gravimetric yield of acid subfraction containing carboxylic acids.

⁶Nonaqueous titration with potassium dimsyl.

⁷Uncertainties are average deviations from duplicate determinations.

⁸Not determined.

⁹Strong acid fraction (4.97 wt % of distillate). Results in Table VIII were obtained on a total (strong + weak) acid fraction (10.4 wt %).

CONCLUSIONS

The highly alkylated nature and generally low concentration of hydroxyl and carboxyl compounds in petroleum, plus the sensitivity of IR to any carbonyl-containing by-products place stringent requirements on any derivatization method employed in conjunction with IR analysis of petroleum. The derivatization procedure developed here comes much closer to meeting these requirements than prior methods.

The main advantages of performing chemical derivatization prior to IR analysis are improved sensitivity and elimination of the interference from water in the determination of hydroxyls, decreased interference from other carbonyl compounds in the determination of carboxylic acids, and an overall reduction in the effects of hydrogen bonding in analysis of other types. These advantages become more significant as the average boiling point of the analytes increases--reaching the point of virtual necessity for distillation residues and very heavy crudes. The main disadvantage is the extra time and effort involved.

Precision in IR analysis was similar for derivatized and underivatized samples or pure compounds. Thus, variation in product yields and recoveries or other errors attributable to the derivatization, per se, was negligible compared to that normally encountered in IR measurements. Results from the present method applied to acid fractions generally were comparable to those from other techniques, including IR without derivatization, and often were slightly lower which is consistent with a lower degree of interference from other acidic compound classes. A comparison of results obtained on derivatized whole fuels/distillates versus their respective acid fractions indicated negligible interference from neutral or basic components as well.

The relative dependence of IR response on structure for derivatives was comparable to that normally encountered for other functional groups--ca. $\pm 10\%$. Trifluoroacetates of 3-methylphenol and 3- or 4-isopropylphenol yield "typical" molar absorptivities and are suitable for calibration of ArOH response. The response of alcohol derivatives is about two-thirds that of ArOH. 2,2,2-Trifluoroethyl esters of petroleum-derived carboxylic acids yield a significantly lower molar absorptivity than any of the pure compounds investigated. At present, an authentic petroleum carboxylic acid concentrate is recommended for calibration of carboxyl response. Although the accuracy

obtainable in functional group analysis of unknown, complex mixtures like petroleum is inherently limited by their variable composition, which in turn affects their average IR response, it is nevertheless adequate for the vast majority of potential applications and is more cost effective than many competing techniques.

Future work is aimed at extending this approach to analysis of acidic nitrogen compounds and to determination of hydroxyls and carboxyls in distillation residues. In the case of very high boiling materials, the main limitations are deficiencies in separation methods and independent analytical methods needed for verification of results from the current method rather than inadequacies of the method itself.

REFERENCES

1. Sleevi, P. S., T. E. Glass, and H. C. Dorn. *Anal. Chem.*, v. 51, 1979, p. 1931.
2. Dorn, H. C., P. S. Sleevi, K. Koller, and T. E. Glass. *Am. Chem. Soc., Div. of Fuel Chem. Prepr.*, v. 24, No. 2, 1979, p. 301.
3. Burke, F. P., R. A. Winschel, and G. A. Robbins. *Recycle Slurry Oil Characterization - Final Report: Period Oct. 1980 - March, 1985*, DOE Contract No. DE-AC22-80PC30027, March 1985.
4. Spratt, M. P., and H. C. Dorn. *Anal. Chem.*, v. 56, 1984, p. 2038.
5. Manatt, S. L. *J. Am. Chem. Soc.*, v. 88, 1966, p. 1323.
6. Rafii, E., R. Faure, L. Lena, E.-J. Vincent, and J. Metzger. *Anal. Chem.*, v. 57, 1985, p. 2854.
7. Dereppe, J.-M., and B. Parbhoo. *Anal. Chem.*, v. 56, 1984, p. 2740.
8. Dewalt, C. W., Jr., and R. A. Glenn. *Anal. Chem.*, v. 24, 1952, p. 1789.
9. Blom, L., L. Edelhausen, and D. W. Van Krevelen. *Fuel*, v. 36, 1957, p. 135.
10. Ignasiak, T., O. P. Strausz, and D. S. Montgomery. *Fuel*, v. 56, 1977, p. 359.
11. Durie, R. A., and S. Sternhell. *Aust. J. Chem.*, v. 12, 1959, p. 205.
12. Tooke, P. B., and A. Grint. *Fuel*, v. 62, 1983, p. 1003.
13. Kuehn, D. W., R. W. Snyder, A. Davis, and P. C. Painter. *Fuel*, v. 61, 1982, p. 628.

14. Painter, P. C., R. W. Snyder, M. Starsinic, M. M. Coleman, D. W. Kuehn, and A. Davis. *Appl. Spectros.*, v.35, 1981, p. 475.
15. Green, J. B., G. P. Sturm, Jr., J. W. Reynolds, J. S. Thomson, S. K.-T. Yu, R. D. Grigsby, S. Y. Tang, J. Y. Shay, D. W. Hirsch, and V. Sanchez. *Analysis of Heavy Oils: Method Development and Application to Cerro Negro Heavy Petroleum. Preliminary Separation and Analysis of Acid, Base, Saturate, and Neutral-Aromatic Fractions*; U.S. DOE Contract No. DE-FC22-83FE60149, NIPER Topical Report No. 161, May 1988.
16. Osawa, Y., and J. W. Shih. *Fuel*, v. 50, 1971, p. 53.
17. Robbins, G. A., R. A. Winschel, F. P. Burke. *Am. Chem. Soc., Div. of Fuel Chem. Prepr.*, v. 30, No. 4, 1985, p. 155.
18. Moschopedis, S. E., and J. G. Speight. *Fuel*, v. 55, 1976, p. 187.
19. Cannon, S. A., C. J. Chu, R. H. Hauge, and J. L. Margrave. *Fuel*, v. 66, 1987, p. 51.
20. Helm, R. V., and J. C. Petersen. *Anal. Chem.*, v. 40, 1968, p. 1100.
21. Cogswell, T. E., J. F. McKay, and D. R. Latham. *Anal. Chem.*, v. 43, 1971, p. 645.
22. McKay, J. F., T. E. Cogswell, J. H. Weber, and D. R. Latham. *Fuel*, v. 54, 1975, p. 50.
23. Bunger, J. W., K. P. Thomas, and S. M. Dorrence. *Fuel*, v. 58, 1979, p. 183.
24. Liotta, R., G. Brons, and J. Isaacs. *Fuel*, v. 62, 1983, p. 781.
25. Liotta, R. *Fuel*, v. 58, 1979, p. 724.
26. Kawahara, F. W. *Anal. Chem.*, v. 40, 1968, p. 2073.
27. Smith, R. V., and S. L. Tsai. *J. Chromatogr.*, v. 61, 1971, p. 29.
28. Brooks, J. B., C. C. Alley, and J. A. Liddle. *Anal. Chem.*, v. 46, 1974, p. 1930.
29. Alley, C. C., J. B. Brooks, and G. Choudhary. *Anal. Chem.*, v. 48, 1976, p. 387.
30. Parish, R. C., and L. M. Stock. *J. Org. Chem.*, v. 30, 1965, p. 927.
31. Tedder, J. M. *Chem. Rev.*, v. 55, 1955, p. 787.
32. Darbre, A. *Handbook of Derivatives for Chromatography*; Blau, K., King, G. S., Eds.; Heyden Press: Philadelphia, PA, 1978; chapter 2.

33. Blau, K.; King, G. S.. Handbook of Derivatives for Chromatography; Blau, K., King, G. S., Eds.; Heyden Press: Philadelphia, PA, 1978; chapter 3.
34. Bellamy, L. J., and R. L. Williams. J. Chem. Soc., 1957, p. 4294.
35. Hewitt, C. D., and M. T. Silvester. Aldrichimica Acta, v. 21, No. 1, 1988, p. 3.
36. Grizzle, P. L., J. B. Green, V. Sanchez, E. Murgia, and J. Lubkowitz, Am. Chem. Soc., Div. Petrol. Chem., Prepr., v. 26, 1981, p. 839.
37. Green, J. B., P. L. Grizzle, J. S. Thomson, R. J. Hoff, and J. A. Green. Fuel, v. 64, 1985, p. 1581.
38. Green, J. B., R. J. Hoff, P. W. Woodward, and L. L. Stevens. Fuel, v. 63, 1984, p. 1290.
39. Green, J. B., B. K. Stierwalt, J. A. Green, and P. L. Grizzle. Fuel, v. 64, 1985, p. 1571.
40. Green, J. B. J. Chromatogr., v. 358, 1986, p. 53.
41. Green, J. B., J. S. Thomson, S. K.-T. Yu, C. A. Treese, B. K. Stierwalt, and C. P. Renaudo. Am. Chem. Soc., Div. Fuel Chem., Prepr., v. 31, No. 1, 1986, p. 198.
42. Green, J. B., P. L. Grizzle, J. S. Thomson, J. Y. Shay, B. H.; Diehl, K. W. Hornung, and V. Sanchez. Analysis of Heavy Oils: Method Development and Application to Cerro Negro Heavy Petroleum. Distillation and Determination of Routine Chemical/Physical Properties; U.S. DOE Contract No. DE-FC22-83FE60149, NIPER Topical Report No. 160; February 1988.
43. Wood, K. V.; C. E. Schmidt, R. G. Cooks, and B. D. Batts. Anal. Chem., v. 56, 1984, p. 1335.
44. Dzidic, I., A. C. Somerville, J. C. Raia, and H. V. Hart. Anal. Chem., v. 60, 1988, p. 1318.
45. Cross, A. D., and R. A. Jones. Practical Infrared Spectroscopy, 3rd Ed.; Butterworths Ltd.: London, 1969; 38-42.
46. Cross, L. H., and A. C. Rolfe. Trans. Faraday Soc., v. 47, 1951, p. 354.
47. Hampton, R. R., and J. E. Newell. Anal. Chem., v. 21, 1949, p. 914.
48. Jones, R. N., D. A. Ramsay, D. S. Keir, and K. Dobriner. J. Am. Chem. Soc., v. 74, 1952, p. 80.
49. Allen, D. T., D. W. Grandy, K.-M. Jeong, and L. Petrakis. Ind. Eng. Chem. Process Des. Dev., v. 24, 1985, p. 737.

50. Seifert, W. K. Progress in the Chemistry of Organic Natural Products, vol. 32; Herz, W., Grisebach, H., Kirby, G. W., Eds.; Springer-Verlag: New York, 1975, pp. 1-49.
51. Ross, A. M., D. L. Whalen, S. Eldin, and R. M. Pollack. J. Am. Chem. Soc., v. 110, 1988, p. 1981.
52. Keeffe, J. R., A. J. Kresge, and Y. Yin. J. Am. Chem. Soc., v. 110, 1988, p. 1982.

**DO NOT MICROFILM
THIS PAGE**

(This page intentionally left blank.)

APPENDIX 2

NMR-CHEMICAL DERIVATIZATION METHOD FOR DETERMINATION OF ACIDIC FUNCTIONAL GROUPS

APPENDIX 2

NMR-CHEMICAL DERIVATIZATION METHOD FOR DETERMINATION OF ACIDIC FUNCTIONAL GROUPS

by \

Daryl A. Doughty and James W. Vogh

Introduction

One of the established methods for determining the different functional groups present in petroleum fractions is nuclear magnetic resonance (NMR) spectroscopy using derivatization of the functional groups of interest with a suitable NMR-active tag. Various NMR-active nuclei incorporated into different derivative structures have been used such as ^{19}F , ^{29}Si , ^{119}Sn , ^{31}P , as well as ^1H and ^{13}C (1-8)*. This list is not meant to represent a complete search of the relevant literature but only to illustrate the possibilities of this approach. The methods based on ^{19}F have been used to determine the trifluoroacetyl derivatives of hydroxyaromatics, alcohols, thiols, and amines (1,4) and the p-fluorobenzoyl derivatives of alcohols, hydroxyaromatics, carboxylic acids, amines and thiols (2,3). The ^{19}F methods apparently are not quantitative with nitrogen functionalities such as carbazole. A method using ^{29}Si NMR with trimethylsilyl derivatives of hydroxyaromatics and carboxylic acids from petroleum and asphaltenes has been reported (4,5), but the quantitative response to other functional types such as alcohols, carbazoles, thiols, and amines has not been established. A method using ^{119}Sn NMR of tributyl tin derivatives of hydroxyaromatics, carboxylic acids, thiols, and alcohols appeared very promising (6). However, testing in our laboratory revealed very little response to important nitrogen functional groups such as carbazoles or indoles (9). A recently reported method used ^{31}P NMR of diphenylphosphinyl derivatives to determine hydroxyaromatics in coal liquids (7). This method also appeared to be quantitative for alcohols and some weak N-H bases but did not react with carboxylic acids, and results on carbazoles or thiols were not reported.

*Underlined numbers in parentheses refer to items in the list of references at the end of this appendix.

All of the derivatization methods considered so far have a serious limitation in that they do not quantitatively respond to one or more important classes of functional groups commonly found in acidic petroleum fractions. A promising method based on ^{13}C -enriched methyl derivatives of acidic hetero-atoms found in petroleum fractions (8) has been expanded in our laboratory into a procedure which appears to respond to all important functional classes and offers excellent discrimination between different functionalities such as phenols (including hindered phenols), carboxylic acids, thiols, aromatic amides, indoles, carbazoles, and benzylic hydrogen activated by neighboring electronegative groups (10). Of the above, carboxylic acids typically react to about 70% conversion while the others are essentially completely methylated. Other work indicated reaction of aliphatic alcohols and amides to about 25-50% completion under the standard conditions. By dividing the sample and methylating half with ^{13}C -enriched methyl iodide and the other half with normal (^{12}C) methyl iodide, a side-by-side comparison of the NMR spectra can yield the total concentration of the various functionalities within the above conversion limitations. The discrimination between the various functional types is enhanced by using the two-dimensional NMR experiment correlating the $^{13}\text{C}/^1\text{H}$ chemical shifts (CHSHF) of the methylated functional groups.

Experimental

Nucleophilic aliphatic substitution reactions provide procedures for alkylation of acidic groups, and convenient methods have been developed for this reaction (8,11,12). Based on these methods, a standard procedure was developed for a wide variety of acidic compounds. The samples (weighed to provide about 0.2 gram of product) were combined with about 2 equivalents of solid potassium hydroxide in about 4 mL 1-methyl-2-pyrrolidinone. To this, about 20 percent excess of carbon-13 methyl iodide was added. After thorough mixing, it was held at 40° C for one hour. It was then poured into water and extracted with ethyl ether to obtain the product. Essentially quantitative conversion was obtained for compounds such as indole, carbazole, phenols (including 2-naphthol and 2,6-di-tert-butyl-4-methylphenol), thiols, and aromatic amides. Also, compounds with benzylic hydrogen activated by neighboring electronegative groups, such as fluorene and oxindole, were

completely converted to the methylated form. Carboxylic acids are relatively slow reacting, and myristic acid required a 100 percent excess of methyl iodide to reach 95 percent conversion under the standard 40° C and one hour reaction conditions. Aliphatic alcohols and amides were converted at about 25 to 50 percent under the standard reaction conditions.

The above methylation procedure using ^{13}C -enriched methyl iodide (99% + $^{13}\text{CH}_3$) was applied to of the total acid fraction from a 370-535° C (700-1000°F) distillate of Wilmington, CA, petroleum and to the first five acid subfractions from further fractionation of this acid fraction. The sixth acid subfraction was not derivatized because of limited sample size. Samples of these same fractions were also methylated using normal methyl iodide (1.1% $^{13}\text{CH}_3$; 98.9% $^{12}\text{CH}_3$). Each sample was dissolved in deuterochloroform (CDCl_3 ; 99.6% D) using tetramethylsilane (TMS) as the internal chemical shift reference. Four types of NMR experiments were run on each of the $^{13}\text{CH}_3$ derivatized samples using a JEOL GX-270 FT-NMR spectrometer operating at 270.15 MHz for ^1H and 67.94 MHz for ^{13}C : a proton NMR experiment (45° pulse, 5 sec. pulse delay, 64 pulse summation); a quantitative ^{13}C NMR experiment (gated-decoupling of protons during signal acquisition, 30° pulse, 20 sec pulse delay, 3200 pulse summation); a DEPTD experiment (Distortionless Enhancement by Polarization Transfer with proton Decoupling) to differentiate the methyl carbon signals (135° pulse (θ), 5 sec pulse delay, 600 pulse summation); a CHSHF (Carbon Hydrogen SHIfT correlation) experiment correlating the ^1H chemical shift with the ^{13}C chemical shift (^1H : 1500 Hz, 128 points; ^{13}C : 4800 Hz, 1024 points; 192 pulse summation each ^1H point, 1.893 sec pulse delay). The first three experiments were also run on each of the $^{12}\text{CH}_3$ derivatized samples.

Results

Table 1 shows the ^1H and ^{13}C chemical shifts of the $^{13}\text{CH}_3$ group for nine model compounds methylated using ^{13}C -enriched methyl iodide together with the methylation yield based on ^{13}C peak integrals. The uncertainty in the yields is about $\pm 7\%$. Several of the methylated compounds contained methyl peaks from side products apparently formed during methylation. These have been identified where possible. These were chosen because they represent possible functional structures present in petroleum acidic classes.

TABLE 1. - Proton (^1H) and carbon-13 (^{13}C) chemical shifts of methylated model compounds

Compound	$\delta(^{13}\text{C})^a$, ppm	$\delta(^1\text{H})^a$, ppm	Methylation Yield, %
Methyl tolyl sulfide	16.5 43.5(4%)	2.40 2.63 (DMSO Imp.)	95
9-Hydroxyfluorene (9-methyl)	26.5	1.67 ($-\overset{ }{\text{C}}\text{CH}_3$)	95
(9-methoxy) Fluorene (9,9-dimethyl)	51.5 27.0 18.0 (6.5%)	2.73 ($-\text{OCH}_3$) 1.46 1.48 (Imp.)	84
N-methylcarbazole	28.5	3.75	96
N-methylindole	32.5	3.48	96
N-methyl-N-phenylvaleramide	37.5	3.22	95
N-methylindazole (1-N)	35.0 (80%)	3.95	100
(2-N)	39.7 (20%)	4.05 (rearrangement)	
Myristic acid (methyl ester)	51.5	3.62	90
2-Naphthyl methyl ether	55.2	3.85	96

^aChemical shifts referenced to internal TMS, $\delta(\text{TMS}) = 0.00$

Table 2 shows the elemental composition data for acid subfractions and the whole acid fraction obtained from a Wilmington 370-535° C distillate. The results are expressed as mole fraction of each element. Oxygen was determined by difference and so is subject to larger uncertainty. Also shown in table 2 is the subfraction yield determined from the mass balance over the separation.

TABLE 2. - Mole fraction elemental composition

Fraction Yield, Wt. %	Sample	C	H	N	S	O (diff.)
16.2	Fraction 1	0.4201	0.5581	0.0118	0.0009	0.0091
18.8	Fraction 2A	0.4267	0.5518	0.0137	0.0005	0.0073
29.3	Fraction 2B	0.4324	0.5428	0.0141	0.0011	0.0097
9.5	Fraction 3	0.4114	0.5480	0.0075	0.0032	0.0298
25.6	Fraction 4	0.3656	0.5965	0.0017	0.0028	0.0334
0.5	Fraction 5	0.3751	0.5358	0.0039	0.0028	0.0824
	Whole	0.4076	0.5608	0.0097	0.0017	0.0203

The average molecular weight of the first four subfractions was taken to be 365 and the molecular weight of subfraction 4 was taken to be 396. Using the elemental composition from table 2, the average carbon number for each

subfraction was found to be 25.5 so the following empirical formulas were calculated for each subfraction and the total mix:

Fr. 1	$C_{25.5}H_{33.86}N_{0.71}S_{0.05}O_{0.56}$
Fr. 2A	$C_{25.5}H_{32.97}N_{0.82}S_{0.03}O_{0.43}$
Fr. 2B	$C_{25.5}H_{32.00}N_{0.84}S_{0.08}O_{0.57}$
Fr. 3	$C_{25.5}H_{33.97}N_{0.46}S_{0.20}O_{1.83}$
Fr. 4	$C_{25.5}H_{41.62}N_{0.13}S_{0.20}O_{2.32}$
Fr. 5	$C_{25.5}H_{36.41}N_{0.25}S_{0.18}O_{5.61}$
Mix	$C_{25.5}H_{35.09}N_{0.61}S_{0.10}O_{1.28}$

The carbon number will be used later to calculate the average number of functional groups per molecule for the acid subfractions and the total acid fraction.

Figures 1-6 show the CHSHF two-dimensional contour plots of the whole acid and the acid subfractions, respectively. In these figures the individual peaks are shown as closed contours of signal height (intensity) plotted at the coordinates of the $^{13}C/^1H$ chemical shifts referenced to the TMS signal in the upper right corner. The ^{13}C chemical shift is the horizontal axis, and the 1H chemical shift is the vertical axis. Also shown in each figure are horizontal and vertical projections of the peak intensity which represent the proton and carbon-13 spectra, respectively, plotted as chemical shift relative to the TMS peak used as internal chemical shift reference. In figure 1, the three regions of interest for methylated oxygen, nitrogen, and sulfur/benzylic functional groups present in the acid subfractions are labelled. Based in part on results for pure compounds in table 1, the oxygen region was defined as the region from 49-65 ppm (^{13}C) and 2.7-4.2 ppm (1H). Similarly, the nitrogen region was found to extend from 28-49 ppm (^{13}C) and 3.0-4.4 ppm (1H). The sulfur/benzylic region extends from 5-28 ppm (^{13}C) and 1.4-3.0 ppm (1H). Above the sulfur/benzylic region is the region from 10-38 ppm (^{13}C) and 0.5-1.4 ppm (1H) which contains peaks typical of alkyl carbons. The peaks of alkyl carbons alpha to aromatic structures can have 1H shifts up to 3.0 ppm; so peaks from these components could interfere with sulfur/benzylic assignments. These same regions apply to the other figures 2-5.

FIGURE 1. - Two-dimensional CHSHF spectrum of the whole acid fraction from a 700-1000° F Wilmington crude oil distillate.

FIGURE 2. - CHSHF spectrum of the acid subfraction #1 from the acid fraction from the 700-1000° F Wilmington crude oil distillate.

FIGURE 3. - CHSHF spectrum of the acid subfraction #2A from the Wilmington distillate acid fraction.

FIGURE 4. - CHSHF spectrum of the acid subfraction #2B.

FIGURE 5. - CHSHF spectrum of the acid subfraction #3.

FIGURE 6. - CHSHF spectrum of the acid subfraction #4.

The oxygen region may be further subdivided into three subregions based on the ^{13}C chemical shift. The methyl esters of carboxylic acids ($-\text{COOCH}_3$) have ^{13}C shifts from 49-54 ppm with the primary position being 51-52 ppm (^1H chemical shifts are typically 3.6-4.0 ppm). The methylated phenols or hydroxyl groups ($-\text{OCH}_3$) have ^{13}C shifts from 54-59 ppm (^1H shifts are typically 3.5-4.2 ppm for aromatic methoxy groups and 3.2-3.5 ppm for aliphatic methoxy groups). However, hindered phenolic groups ($-\text{OCH}_3(\text{H})$) which have two ortho-substituents exhibit ^{13}C shifts from 59-63 ppm (^1H shifts are similar to those of other methoxy groups). These three subregions seem to be well-defined with essentially no overlap based on the ^{13}C chemical shifts of many compounds (13). However, the methylated model compound 9-hydroxyfluorene had a ^{13}C shift for the $-\text{OCH}_3$ group of 51.5 ppm with a ^1H shift of 2.75 ppm, both outside the typical ranges for the $-\text{OCH}_3$ groups. A series of 9-*n*-alkylfluorene-9-ols has previously been identified in petroleum (14).

Within the nitrogen region those methyls attached to amine type nitrogens have ^1H shifts around 3.0-3.2 ppm while methyls attached to nitrogen in aromatic rings or condensed ring systems have ^1H shifts from 3.4-4.4 ppm. For example, the methylated model compound carbazole has a $^{13}\text{CH}_3$ shift of 28.5 ppm (^{13}C) and 3.75 ppm (^1H). If the ring system has several nearby nitrogens the ^1H shift of the N-methyls is generally toward the higher end of the range.

Within the sulfur/benzylic region, methyl sulfides generally have ^1H shifts from 2.0-2.5 ppm with the aromatic methyl sulfides around 2.4-2.5 ppm. The ^{13}C shifts of methyl sulfides are generally from 10-20 ppm. Benzylic methyls have ^1H shifts typically from 1.4-2.0 ppm.

Figure 1 shows that the Wilmington whole acid contains substantial oxygen and nitrogen methylated classes with very little in the sulfur/benzylic region. Within the oxygen region the most prominent peak is that typical of methyl esters of carboxylic acids at 51.3 ppm/3.62 ppm ($^{13}\text{C}/^1\text{H}$). There is a group of several peaks typical of methylated phenols at 55 ppm/3.8 ppm and a smaller group of peaks typical of hindered methylated phenols at 60 ppm/3.7 ppm, with several smaller peaks from other methylated oxygen classes of intermediate nature.

There is a substantial group of methylated nitrogen classes with carbazole prominent as the peak at the right edge of this region at 28.7 ppm/3.72 ppm. N-methylindole would appear to be outside this group based on the ^1H shift of 3.48 ppm, but N-methylindazole would appear to be a good

representative at 35.0 ppm/3.95 ppm (39.7 ppm/4.05 ppm for the rearrangement product). N-methyl-N-phenylvaleramide also appears to be an unlikely candidate based on the ^1H shift of 3.22 ppm for the methyl protons.

There are only two small peaks in the sulfur/benzylic region that could represent methylated classes. Neither have ^1H shifts that would likely represent methylated sulfur classes. The lack of peaks in this region may be a result of the prominent carboxylic acid ester peak in the oxygen region being used to scale the displayed contours in figure 1. Other peaks are displayed in this and the other two regions in figures 2-6 where lower contours were chosen.

Comparing the Wilmington acid subfractions, whose CHSHF spectra are shown in figures 2-6, several trends may be noted in the oxygen and nitrogen regions. For the oxygen region the prominent peak representing methyl esters of carboxylic acids at 51.3 ppm/3.62 ppm is seen at much reduced amplitude in subfraction 1 (figure 2), almost disappears in subfractions 2A and 2B (in figures 3 and 4), starts to reappear in subfraction 3 (figure 5), and is essentially the only peak present in subfraction 4 (figure 6). It is difficult to accept the possibility that RCOOH functional groups are being spread over this wide a range in the subfractionation scheme. However, any other explanation is only guess work at this time. A common artifact of the CHSHF experiment is the "tails" extending vertically in the ^1H shift direction for prominent peaks when low contours are used to show weaker peaks. These artifacts are evident somewhat in figure 3 and strongly in figures 4-6. For the methylated phenolics, the hindered phenols are most prominent in subfractions 2A and 2B (figures 3 and 4) while the phenols are most prominent in subfractions 2B and 3 (figures 4 and 5). The identity of the peak at 53.0 ppm/4.05 ppm which is present in subfractions 1, 2A (most strongly), and 2B (figures 2-4) is not known.

The nitrogen region is prominent in subfractions 1, 2A, and 2B (figures 2-4), has only a few peaks in subfraction 3 (figure 5) and has disappeared in subfraction 4 (figure 6). The peaks in this region do show considerable variability in intensity and ^{13}C shifts over the three subfractions 1-2B (figures 2-4) implying that the identity of the nitrogen types is changing from fraction to fraction. The peak at 28.7 ppm/3.72 ppm representing methylated carbazole is barely noticeable in subfraction 1 (figure 2), increases in prominence in subfraction 2A (figure 3), is most prominent in

subfraction 2B (figure 4) then fades in subfraction 3 (figure 5). Outside of carbazole there are many species of methylated nitrogen classes evident in the first three subfractions whose exact nature is unknown.

The benzylic/sulfur region contains a few weak peaks, mainly in the benzylic region in subfraction 1 (figure 2), but some at higher ^1H shifts in subfraction 2B and 3 (figures 4 and 5) that could be methylated sulfur classes. The sharp peak at 21 ppm/2.0 ppm in subfractions 2B and 3 (figures 4 and 5) has characteristics more typical of a solvent impurity than that of a methylated acid species.

The CHSHF experiment is inherently not quantitative; so the intensities or integrals of peaks in figures 1-6 cannot be used as a measure of the exact proportions of each acid class present in each sample. Tables 3-6 show in various formats the quantitative results determined for the whole acid fraction and the five subfractions. In table 3 are shown the ^{13}C peak integrals from the quantitative ^{13}C NMR experiments for both the $^{13}\text{CH}_3$ and $^{12}\text{CH}_3$ methylated samples of each subfraction. The integrals are shown for four regions: the aromatic region (110-160 ppm) and the oxygen, nitrogen, and benzylic/sulfur regions previously identified. The aromatic carbon structure has been assumed to be unaltered by the methylation process; so all integrals have been scaled to give the same result for the aromatic region.

TABLE 3. - Quantitative carbon-13 NMR peak integrals

Sample	Arom.	49-65 ppm	28-49 ppm	5-28 ppm	Total
Fract. 1 ($^{13}\text{CH}_3$)	79.8 ^a	124.3	423.6	75.7	703.4
Fract. 1 ($^{12}\text{CH}_3$)	79.8	7.0	56.8	43.8	187.4
Fract. 2A ($^{13}\text{CH}_3$)	79.8	121.6	547.1	49.0	797.5
Fract. 2A ($^{12}\text{CH}_3$)	79.8	4.0	49.8	39.3	172.9
Fract. 2B ($^{13}\text{CH}_3$)	79.8	211.3	506.0	67.5	864.6
Fract. 2B ($^{12}\text{CH}_3$)	79.8	6.2	44.1	36.0	166.1
Fract. 3 ($^{13}\text{CH}_3$)	79.8	608.2	272.0	99.1	1059.1
Fract. 3 ($^{12}\text{CH}_3$)	79.8	4.5	53.6	45.2	183.1
Fract. 4 ($^{13}\text{CH}_3$)	79.8	1511.5	341.0	192.5	2124.8
Fract. 4 ($^{12}\text{CH}_3$)	79.8	33.4	183.3	89.5	386.0
Total Acid ($^{13}\text{CH}_3$)	79.8	480.9	535.0	113.8	1209.5
Total Acid ($^{12}\text{CH}_3$)	79.8	7.4	61.6	48.8	197.6

^aThe integrals for each sample were scaled to make the aromatic integral the same. The aromatic portion of the sample was assumed to be invariant during methylation.

Table 4 shows the relative proportions of the three oxygen subclasses present in each subfraction and the whole acid. As discussed previously, from a qualitative aspect in figures 2-6 and confirmed here quantitatively, hindered phenols are most prominent in the earlier subfractions, phenols are most prominent in the middle subfractions 2B and 3, and carboxylic acids are by far the most prominent in subfraction 4. For the whole acid, carboxylic acids are most prominent with equal amounts of phenols and hindered phenols making up the balance.

TABLE 4. - Quantitative subdivision of oxygen functionalities

Sample	-COOCH ₃	-OCH ₃	-OCH ₃ (H)
Fract. 1	33%	11%	56%
Fract. 2A	30%	12%	58%
Fract. 2B	15%	50%	35%
Fract. 3	19%	64%	17%
Fract. 4	93%	3%	4%
Total Acid	58%	21%	21%

The data in table 3 show the dramatic enhancement of the ¹³C signal in each region caused by the enriched ¹³CH₃ methylation. The natural abundance of ¹³C in normal materials is 1.108%. The enriched ¹³CH₃ signals (99+% ¹³C) are therefore 90 times larger in magnitude than actually present in the samples. By subtracting the ¹²CH₃ integral from the corresponding ¹³CH₃ integral in each region, and dividing the difference by the enrichment factor (90.0), the actual contribution of the methylated acid classes to the normal ¹³C spectrum integral for each subfraction and whole acid can be obtained. These data are shown in table 5. For example, the total ¹³C integral of the ¹²CH₃ methylated sample of subfraction 1 is 187.4 from table 3. Table 5 shows that 5.73 units of this represent the methylated acid classes in this subfraction, which is subdivided into the three regions as shown.

TABLE 5. - Quantitative enhancement corrected for enrichment factor

Sample	49-65 ppm	28-49 ppm	5-28 ppm	Total
Fract. 1	1.30	4.08	0.35	5.73
Fract. 2A	1.31	5.53	0.11	6.94
Fract. 2B	2.28	5.13	0.35	7.76
Fract. 3	6.71	2.43	0.60	9.73
Fract. 4	16.42	1.75	1.14	19.32
Total Acid	5.26	5.26	0.72	11.25

The total integral for each of the $^{12}\text{CH}_3$ methylated samples shown in table 3 represents the total signal from each of the different types of carbon in the sample including the added methyls whose individual contributions are shown in table 5. If we assume that each added methyl represents one functional group and we had the average integral per carbon for each sample, we could determine the number of functional groups per average molecule for each category. The compositional data and the measured molecular weights showed that each subfraction and the whole acid had 25.5 carbons per molecule. Dividing the total integral of the $^{12}\text{CH}_3$ methylated samples by 25.5 will give the average integral per carbon for each sample. Combining this number for each sample with the results in table 5 gives the results in table 6 showing the number of functional groups per average molecule, both total and for each category. For example, the total $^{12}\text{CH}_3$ integral for subfraction 1 is 187.4. Dividing $187.4/25.5$ gives 7.35 integral units per carbon. The total integral for subfraction 1 from table 5 is 5.73 representing added methyls on functional groups. Dividing 5.73 by 7.35 gives 0.780 total functional groups in table 6. Also shown is the balance based on the fraction yield for each subfraction. The measured result for the whole acid is larger than this balance; while the relative contributions of each region are very similar. Figure 7 shows graphically the number of functional groups per molecule for the three categories for each subfraction. Comparing table 6 and figure 7 with the corresponding oxygen, nitrogen, and sulfur heteroatom composition in table 2, the agreement in the trends across the subfractions is striking. This confirms that the heteroatom composition in the acid fraction is strongly correlated with the acidic classes present in the fractions.

a

FIGURE 7. - Number of acid functional groups per molecule for the acid subfractions from the acid fraction from the 700-1000° F Wilmington crude oil distillate.

TABLE 6. - Number of functional groups per average molecule

Sample	49-65 ppm	28-49 ppm	5-28 ppm	Total
Fract. 1	0.177	0.555	0.048	0.780
Fract. 2A	0.193	0.816	0.016	1.024
Fract. 2B	0.350	0.788	0.054	1.191
Fract. 3	0.934	0.338	0.084	1.355
Fract. 4	1.085	0.116	0.075	1.286
Total Acid	0.679	0.679	0.089	1.450
Balance ^a	0.534	0.536	0.054	1.123

^aObtained using the fraction yield (wt %) to get a weighted average.

Using the relative data of table 4 for the distribution of oxygen classes within the three subdivisions and the results from table 6 showing the number of oxygen functional groups per molecule (49-65 ppm), the number of oxygen functional groups per molecule of each of the three types was determined for each subfraction. These results are shown in figure 8 and dramatically illustrate the change in prominence of the three oxygen classes across the subfractions.

Discussion and Conclusions

One apparent discrepancy in the results is the difference in the number of functional groups per molecule found for the whole acid fraction compared to the balance obtained based on the fraction yields as shown in table 6. The whole acid fraction was derivatized and run seven months before the subfractions. Also, a slightly smaller number of pulses were summed to get the final spectrum (2800 to 3200 pulses). Because the total integrals are scaled by the aromatic signal integral and this signal is normally a low amplitude, broad signal, a small change in the baseline correction between the two sets of runs could have a major effect on the apparent aromatic integral and the scaled result. Also, the NMR longitudinal relaxation times (T_1) for the whole acid could be different from that of the individual subfractions because of functional group interactions. This could affect the relative amount of aromatic signal detected because the unprotonated aromatic carbons would have the longest T_1 times and be most affected by these factors. For these reasons the apparent magnitude discrepancy is probably not indicative of a real functional group difference in the two sets of data.

FIGURE 8. - Number of oxygen functional groups per molecule for the acid subfractions from the Wilmington distillate acid fraction.

In tests of the acid subfractionation scheme on model compounds, carboxylic acids partitioned into fraction 4 and carbazole into fraction 2B. The results on the subfractions support this with methylated carboxylic acids most strongly concentrated in subfraction 4 and the methylated carbazole most strongly seen in subfraction 2B. In general, the more acidic classes appear in the later subfractions. However, as shown with the oxygen functionalities in figure 8, there is some spread of the different classes into the adjacent subfractions. Structural variability, including the degree of steric hindrance around the functional group, is probably responsible for the observed overlap. Also, incomplete and/or misassignment of minor peaks in spectra may have increased the apparent overlap in selected cases. Except for subfraction 1, the results show more than one functional group per average molecule. In some cases, both functional groups may significantly affect separation behavior and in others the effect of one of the groups (e.g., hindered $-OCH_3$) may be negligible.

The CHSHF results reveal that numerous subtypes are resolved within each spectral region, particularly in the nitrogen region, whose exact nature is not known. Additional work will be required to identify these other types and/or functional groups present.

In summary, this scheme for the determination of acid class functionalities, while involving several procedures, has the ability to quantitatively determine all major acid classes present in typical petroleum while also showing excellent capability for resolving complex mixtures of subclasses.

References

1. Dorn, H. C., P. S. Sleevi, K. Koller, and T. Glass. Am. Chem. Soc., Div. of Fuel Chem. Prepr., v. 24, No. 2, 1979, p. 301.
2. Spratt, M. P., and H. C. Dorn. Anal. Chem., v. 56, 1984, p. 2038.
3. Spratt, M. P., D. Armistead, E. Motell, and H. C. Dorn. Anal. Chem., v. 57, 1985, p. 359.
4. Dereppe, J.-M., and B. Parbhoo. Anal. Chem., v. 56, 1984, p. 2740.
5. Dereppe, J.-M., and B. Parbhoo. Anal. Chem., v. 58, 1986, p. 2641.
6. Rafii, E., R. Faure, L. Lena, E.-J. Vincent, and J. Metzgar. Anal. Chem., v. 57, 1985, p. 2854.

7. Dadey, E. J., S. L. Smith, and B. H. Davis. *Energy & Fuels*, v. 2, 1988, p. 326.
8. Rose, K. D., and M. A. Francisco. *Energy & Fuels*, v. 1, 1987, p. 233.
9. NIPER Quarterly Technical Report NIPER-253, March 31, 1987, p. 100.
10. OSPR Quarterly Technical Report B06807-17, June 30, 1988.
11. Hearney, H., and S. V. Ley. *Org. Synth.*, v. 54, 1974, pp. 58-60.
12. Pfeffer, P. E., and L. S. Sibert. *J. Org. Chem.*, v. 41, 1976, pp. 1373-9.
13. Breitmaier, E., and W. Voelter. *Carbon-13 NMR Spectroscopy*, 3rd Edition, VCH, New York, NY, 1987.
14. Payzant, J. D., T. W. Mojelsky, T. D. Cyr, D. S. Montgomery, and O. P. Strausz. *Org. Geochem.*, v. 8, 1985, p. 177.

APPENDIX 3
NONAQUEOUS TITRATION OF ACIDS

APPENDIX 3

NONAQUEOUS TITRATION OF ACIDS

by

Judy A. Green

ABSTRACT

A nonaqueous potentiometric titration procedure based on use of potassium dimsyl, the product from reaction of potassium hydride and dimethyl sulfoxide, as a titrant for acidic compounds is described. Because of its strongly basic character, the above titrant effectively neutralizes even very weakly acidic species such as benzologs of pyrrole, benzylic alcohols, and aromatic hydrocarbons with benzylic hydrogens.

INTRODUCTION

Many publications have appeared in the last 30 years describing the titrations of weak acids in nonaqueous solvents employing a variety of solvents and titrants. The two main types of titrants which have been used are alkali metal hydroxides (or alkoxides) and quaternary alkylammonium hydroxides. Alcoholic KOH is used in the ASTM method for determining strong acid number (D 664). This method will titrate moderately weak acids such as phenol, but better results are achieved with sodium or potassium methoxide in benzene-methanol. The most widely used titrant for acids in nonaqueous solutions is tetrabutylammonium hydroxide in 2-propanol or benzene-methanol. One advantage of this titrant is that in almost every case the tetrabutylammonium salt of the titrated acid is soluble in the solvent used (sodium or potassium salts of titrated acids frequently form gelatinous precipitates). Also, good potentiometric curves are obtained using ordinary glass and calomel electrodes since no "alkali error" is produced. Quaternary alkylammonium hydroxides have been used to titrate a variety of acids including hydroxyaromatics, carboxylic acids, enols, imides, sulfonamides, thiols, and carbazole. Dutta and Holland (1)* reported that indole homologs (aqueous $pK_a \geq 12$) were the weakest acid group to titrate quantitatively.

*Underlined numbers in parentheses refer to items in the list of references at the end of this appendix.

Less frequently, much stronger bases have been used as titrants. These include lithium aluminum amides, potassium tert-butoxide, and the sodium and potassium salts of dimethylsulfoxide ("Na-dimsyl" and "K-dimsyl"). The methylsulfonyl carbanion

is known to be strongly basic and should be an effective titrant for very weak acids. The majority of the reported work using the dimsyl titrants has used visual indicators (e.g., triphenylmethane) to determine equivalence points. Potentiometric titrations are somewhat more difficult since electrode response in dimethyl sulfoxide (DMSO) can be sluggish, especially at high pH values. There are also potential problems with precipitate formation and "alkali error" interference. Modifications in conventional apparatus and solvent systems required to overcome these problems are described herein. Also, potassium dimsyl is shown to be suitable for titration of compounds covering a wide range of acidity, including those typically encountered in petroleum.

Description of the Method and Experimental Procedures

Materials: American Burdick and Jackson (Muskegon, MI) high purity DMSO and EM Sciences Omnisolv DMSO (Cherry Hill, NJ) were used as solvent for the titrant and samples with no further purification. Potassium hydride (obtained as a 35% by weight dispersion in mineral oil), p-toluenesulfonic acid monohydrate, silver perchlorate hydrate, lithium perchlorate, triphenylmethane, and 18-crown-6 ether were used as received from Aldrich Chemical Company (Milwaukee, WI). Benzoic acid used for standardization was obtained from the National Bureau of Standards (Washington, DC). 1,2,3,4-Tetrahydrocarbazole (THC), used as a weak acid standard, was used as received from Aldrich (99%).

Apparatus: Titrations were performed using a custom-made all-Teflon buret with a stainless steel stopcock. All beakers, flasks, and bottles used were also made of Teflon. A Mettler automatic titration system (DV10 buret and

DK15 control module) was used to dispense titrant and monitor the potentiometric readings. The reference electrode used was a Corning double junction model from Corning Glass Works, Corning, NY (Model No. 476067), with a Ag/AgCl inner reference electrode. The outer jacket contained a solution of 0.1 M LiClO_4 in DMSO which prevented the aqueous inner solution from contacting the sample. The measuring electrode was an Orion glass pH electrode (Model No. 91-01 from Orion Research, Inc., Boston, MA) with Ag/AgCl internals. The electrode was modified for use in DMSO using a technique similar to that described by Ritchie and Uschold (2). The electrode was disassembled, and the aqueous internal solution was replaced with 0.2 M silver perchlorate hydrate and 0.006 M p-toluenesulfonic acid monohydrate in DMSO. The silver wire was polished with steel wool, and the electrode was reassembled and taped where it had been cut open at the top. This electrode was found to respond much better in DMSO than an unmodified electrode.

A dry-box was used to house the titration apparatus, titrant, and samples. A continuous flow of argon (or nitrogen) through the dry-box protected the titrant from exposure to moisture and carbon dioxide in room air. A desiccant (phosphorus pentoxide) was used to further reduce moisture content inside the box.

Preparation of Titrant: The titrant was prepared inside the dry-box by reacting potassium hydride with DMSO. A small amount (approximately 1.5-2.0 mL) of the potassium hydride in mineral oil was stirred (using a magnetic stirrer) in a 500 mL Teflon bottle while DMSO was added very slowly (a few drops at a time). When the reaction was complete, 20 g of 18-crown-6 ether and a small amount of triphenylmethane were added, and the titrant was diluted to 500 mL by adding additional DMSO. The titrant strength usually ranged from 0.01 to 0.03 N. The crown ether served as a chelating agent for the potassium ion (also used by Kolthoff, et al. (3) with potassium tert-butoxide titrant). This appeared to have a stabilizing effect on the titrant and also prevented formation of potassium salts during titration. The triphenylmethane gave the titrant a red color and thus provided a visual check for the presence of the dimsyl ion. After the Teflon tube leading to the buret was placed in the titrant, a layer of mineral oil was poured on top to serve as further

protection from moisture. The bottle containing the titrant was placed in a metal canister under a constant argon (or nitrogen) flow. The titrant was standardized using benzoic acid and THC.

Titration Procedure: Pure compounds and petroleum fractions were weighed using a microbalance and placed in the dry box where they were dissolved in 1 mL of benzene. Samples which were difficult to dissolve, such as those from higher boiling distillates and residues, were heated (with additional benzene if required) in a sonic bath to insure complete dissolution. Prior to titration, samples were transferred to 50 mL Teflon beakers, and 29 mL of DMSO and a magnetic stir bar were added. Diluted samples were purged with argon (or nitrogen) for approximately 30 seconds. The beakers were placed inside a covered glass beaker under a constant flow of argon. Samples were then titrated with potassium dimsyl in DMSO using the Mettler automatic titration system. The potentiometric readings were monitored using the electrodes described previously. The recorder (Kipp and Zonan BD41) output provided a potentiometric curve and first derivative curve for equivalence point determinations.

Equivalence points for standards and samples were corrected for the volume of titrant required to bring a 29 mL DMSO/1mL benzene blank to the appropriate equivalence potential. Typically, minor amounts of more weakly basic contaminants (e.g., KOH) are formed during preparation of the titrant; these contribute to the effective normality of the titrant during titration of relatively strong acids like benzoic acid, but not weak acids such as THC. Thus, use of both acids as standards enables determination of a normality for potassium dimsyl alone as well as a normality for total bases (potassium dimsyl + KOH). The appropriate normality is then used to calculate the amount of stronger or weaker acids present in the samples. Titration of the stronger acids by KOH or other weak bases produces water or other weak acids, which are subsequently titrated by potassium dimsyl along with any weaker acids in the sample. However, this KOH-induced error is self-cancelling, as discussed below.

Figure 1A shows a typical titration curve for benzoic acid plus THC. Contributions of KOH or other basic contaminants to the apparent normality calculated from titration of benzoic acid (EP_1),

are exactly cancelled during subsequent titration of the very weak acid THC (EP_2).

Thus, the normality of potassium dimsyl proper (N_D) may be calculated from the combined endpoints ($EP_1 + EP_2$) and that including KOH or other contaminants (N_T) is calculated from EP_1 . $N_T \geq N_D$. During titration of petroleum fractions, e.g., figure 1B, N_T is used for calculation of acids exhibiting acidities comparable to that of benzoic acid (EP_1) and N_D is used in the calculation of total acids ($EP_1 + EP_2 + EP_3$). In the case where only two endpoints are observed, the proportion of weaker acids is simply calculated as the difference between total and strong acids. When three endpoints are observed, as in figure 1B, strong acids are calculated from EP_1 (mL titrant $\times N_T$), weak acids are calculated from EP_2 (mL titrant $\times N_D$) and very weak acids are calculated by difference (total - (strong + weak)).

RESULTS

Table 1 shows half neutralization potentials (HNPs) and percent titrated results for representative pure compounds using the above procedure. Potassium dimsyl quantitatively titrates a wide variety of acids ranging from carboxylic acids to very weak acids such as amides, pyrrolic benzologs and hydrocarbons with benzylic hydrogens (e.g., fluorene).

As indicated in figure 1, HNP corresponds to the electrode potential midway through titration of a given compound or compound type. HNP indicates relative acidity in DMSO in a manner analogous to pK_a for aqueous media. However, the effect of solvent (DMSO versus water) on apparent acidity is significant (4). For example, figure 2 shows the correlation between HNP and pK_a for compounds where both data are available. Interestingly, three of the major types of compounds titrated--carboxylic acids, hydroxyl compounds and acidic nitrogen compounds--cluster in three distinct groups in the figure, and yield linear correlations with quite similar slopes. Thus, pK_a and HNP correlate well within a given compound class, but dissimilar classes may exhibit much different relative acidities in water versus DMSO. For example, the acidities of hydroxyl and nitrogen compounds are widely separated in water but overlap in DMSO.

FIGURE 1. - Representative titration curves of the standard and a whole acid concentrate. See text.

FIGURE 2. - pK_a (aqueous) versus HNP in DMSO for several acids (A - phthallic acid, B - dimethylmalonic acid, C - succinic acid, D - benzoic acid, E - benzimidazole, F - 1-naphthol, G - 4-phenylimidazole, H - phenol, I - hydroquinone, J - o-cresol, K - imidazole, L - pyrrole.

TABLE 1. - Half-neutralization potentials (HNP) and % titrated results for pure compounds

Compound	HNP (mV)	% Titrated	Reported % Purity
Benzenesulfonic Acid	+300	95	? (Eastman)
Phthalic Acid (1st e.p.)	+120	106	99 (Aldrich ²)
Succinic Acid (1st e.p.)	+10	103	99 (Aldrich)
Salicylic Acid	+8	99.0	? (Fisher ³)
Benzoic Acid ¹	-60	(assumed 100)	NBS
2,2'-Dihydroxybiphenyl	-75	99.0	? (Aldrich)
Stearic Acid	-85	99.7	? (Fisher)
1,1'-Bi-2-naphthol (1st e.p.)	-92	97.1	99 (Aldrich)
Anthrone	-110	99.0	?
Phthalic Acid (2nd e.p.)	-260	93.1	99 (Aldrich)
2,3-Dihydroxypyridine (1st e.p.)	-265	99.5	98 (Aldrich)
Succinic Acid (2nd e.p.)	-270	96.8	99 (Aldrich)
2,6-Di- <i>t</i> -butyl-4-methylphenol	-290	96.9	99+ (Aldrich)
4-Phenylimidazole	-320	94.3	?
9-Hydroxyfluorene	-370	95.9	97+ (Aldrich)
4,4'-Dihydroxybiphenyl	-380	198.0 ⁶	? (Pfaltz & Bauer, Inc. ⁴)
<i>o</i> -Cresol	-410	99.9	>99.5 (Fluka ⁵)
2,4,6-Trimethylphenol	-425	99.0	>98 (Fluka)
Imidazole	-457	99.0	99 (Aldrich)
Carbazole	-467	100.0	98 (Fluka)
Indole	-475	99.0	99+ (Aldrich)
Hydroquinone	-485	101	? (Fisher)
Fluorene	-500	91	98 (Chem Service, Media, PA)
1,2,3,4-Tetrahydrocarbazole ¹	-520	(assumed 99.0)	99 (Aldrich)
Acetanilide	-545	96.2	? (NBS)
1,1'-Bi-2-naphthol (2nd e.p.)	-662	104	99 (Aldrich)
9-Fluorenone	-670	102	98 (Aldrich)
Diphenylamine	-670	104	? (Eastman)
2,3-Dihydroxypyridine (2nd e.p.)	-695	95.2	98 (Aldrich)
Cyclopentanone	-710	97.1	? (MCB)
Iminostilbene	-735	94.2	97 (Aldrich)
Acetamide	-745	94.7	>99 (Fluka)
Urea	no endpoint		
Sulfolane	no endpoint		

¹Used as standards.

²Aldrich Chemical Co. (Milwaukee, WI).

³Fisher Scientific Co. (Fair Lawn, NJ).

⁴Pfaltz & Bauer, Inc. (Waterbury, CT).

⁵Fluka, AG.

⁶Both hydrogens titrated together, thus the high value.

HNP's for the carboxylic acids are well resolved, except for titration of the second hydrogen in dicarboxylic acids (points A₂ and C₂, figure 2), from the other two compound classes. Thus, the first equivalence point in titration of petroleum acid concentrates results primarily from neutralization of carboxylic acids, and the second equivalence point measures the combined concentration of hydroxyl compounds, nitrogen-containing acids, and other weakly acidic types. However, dicarboxylic acids can contribute equally to both equivalence points and, if present in significant quantities, can cause the titration method to underestimate total carboxyls and overestimate weak acids. Similarly, aromatic ketones analogous to anthrone and thiols (4) exhibit exceptional acidity in DMSO and, if present, can co-titrate with carboxylic acids.

Fluorene, indene (4) and analogous aromatic hydrocarbons exhibit acidities in DMSO comparable to pyrrolic benzologs. Thus, results from titration of whole crudes, distillates, or residues reflect concentrations of those types as weak acids.

To date, the main applications of the method have been in determination of equivalent weights and carboxylic acid contents of whole acid concentrates and subfractions (see Chapters 1 and 2, and the main body of this chapter). Equivalent weights are typically used as estimates of average molecular weight since the proportion of molecules having multiple groups of sufficient acidity to titrate appears to be small in most petroleum and syncrude fractions. As noted above, only carboxylic acids exhibit an endpoint sufficiently well resolved from other acidic classes in titrations of whole acid concentrates or other relatively crude fractions. However, in special cases (e.g., subfractions) additional classes can be determined and/or other information may be obtainable from titration data. For example, titration of SRC-II >325° C strong acid subfraction 5, which contains predominantly dihydroxy-aromatic compounds (see main body of this chapter), revealed four endpoints: 0.24 meq/g (+100 mV), 3.00 meq/g (-195 mV), 2.51 meq/g (-380 mV) and 0.07 meq/g (-580 mV). The extremely low magnitude of the last endpoint indicates a very low proportion of di-o-substituted species, since 2,2'-dihydroxybiphenyl, 1,1'-bi-2-naphthol, and 2,3-dihydroxypyridine all exhibited secondary equivalence points at HNP's more negative than -600 mV (table 1). Also, the observed distribution of compounds over two main equivalence points is

consistent with two primary orientations of hydroxyl groups, e.g., meta and para. However, the above case is fortuitous because of the availability of supporting information and the prominence of one class in the subfraction.

DISCUSSION

The main advantage of potassium dimsyl is its ability to titrate very weak acids, which enables determination of accurate equivalent weights. Its primary disadvantage in turn is its high reactivity, which necessitates rigorous exclusion of atmospheric water and construction of an all-teflon titrant storage and delivery apparatus. Data precision is comparable to other microtitration procedures (ca. $\pm 5\%$), and is largely limited by the ability to determine endpoints via first derivative plots or other methods.

REFERENCES

1. Dutta, P. K., and R. J. Holland. Fuel, v. 62, 1983, p 732.
2. Ritchie, C. D., and R. E. Uschold. J. Amer. Chem. Soc., v. 89, 1967, p 1721.
3. Kolthoff, I. M., and M. K. Chantooni. Anal. Chem., v. 51, 1979, p 1301.
4. Bordwell, F. G. Acc. Chem. Res., v. 21, 1988, p. 456.

**DO NOT MICROFILM
THIS PAGE**

(This page intentionally left blank.)

APPENDIX 4

**RETENTION INDICES, RELATIVE RESPONSE FACTORS,
AND MASS SPECTRA OF TRIFLUOROACETATE ESTERS OF
PHENOLIC COMPOUNDS DETERMINED BY CAPILLARY GC/MS**

APPENDIX 4

RETENTION INDICES, RELATIVE RESPONSE FACTORS, AND MASS SPECTRA OF TRIFLUOROACETATE ESTERS OF PHENOLIC COMPOUNDS DETERMINED BY CAPILLARY GC/MS

by

Shirley K.-T. Yu, Robert P. Vrana and John B. Green

ABSTRACT

GC retention indices of trifluoroacetyl esters of hydroxyaromatic compounds on a methylsilicone column are reported along with total ion current GC/MS response factors relative to 4-fluorophenyl trifluoroacetate. Experimental procedures for data acquisition and preparation of trifluoroacetyl esters are provided.

INTRODUCTION

The inherent problems associated with analysis of phenolic compounds by gas chromatography/mass spectrometry (GC/MS) are poor GC resolution and difficulties in distinguishing mass spectra of isomers. For example, White and Li (1)* reviewed GC separations of underivatized (C_0 - C_2)-phenols and found that complete separation of all isomers required the use of highly specialized stationary phases. The best separations were obtained with long-chain phthalate ester stationary phases treated with strong acids, such as phosphoric acid. However, these columns typically exhibit maximum temperature limits of 135° C, which greatly limits their range of applicability. Even the best commercially available capillary columns have difficulty resolving relatively simple alkylphenol mixtures. For example, the polyethylene glycol column employed by White and Li did not resolve 4-methylphenol/2,5-dimethylphenol, and 3,5-dimethylphenol/4-ethylphenol.

By forming trifluoroacetyl derivatives of phenols, Shulgin (2) was able to improve their GC resolution dramatically. Nearly complete resolution of all possible methylphenol isomers up to pentamethylphenol was obtained with a

*Underlined numbers in parentheses refer to items in the list of references at the end of this appendix.

2-m packed column. The mass spectra of a limited number of trifluoroacetate esters of phenolic compound were reported by Saxby (3), who found that they typically exhibited strong molecular and significant fragment ions corresponding to losses of COCF_3 and $(\text{CO} + \text{COCF}_3)$. With the exception of these two papers, little information existed on either the GC or MS characteristics of trifluoroacetate esters of hydroxyl compounds prior to a preliminary evaluation of this approach conducted in this laboratory (4,5).

This appendix is divided into four sections. The first section compares mass spectra and retention indices of acylated* hydroxyaromatics (ArOH) with those underivatized ArOH . The second section discusses GC resolution using different columns for acylated ArOH . The third section compares mass spectra generated in our laboratory with standard spectra in the MS library supplied with the instrument. The fourth section compiles GC retention indices and relative GC/MS response factors for individual ArOH derivatives. The information contained in the fourth section comprises a portion of the current NIPER data base used for qualitative identification of ArOH derivatives in fuels and other complex matrices. It is hoped that making these data available to others will spur development and acceptance of this approach.

EXPERIMENTAL

The phenolic compounds covered in this report were either obtained from commercial sources, synthesized in-house, or present in actual fuel samples.

Preparation of Derivatives

The derivatization procedure was published previously (6) but is reproduced below for the reader's convenience.

A known weight of material, typically 5-10 mg, was prepared for acylation by addition of 4 mL of a solution of 0.25 M 4-dimethylaminopyridine (DMAP) in dichloromethane. Acylation was carried out by simply bubbling the solution with trifluoroacetyl chloride (TFACl) gas for 30 min at room temperature. Excess reagents and trifluoroacetic acid produced as a by-product were removed

*Throughout this appendix, the term "acylation" refers specifically to formation of trifluoroacetyl esters.

via extraction with 20 mL of aqueous 0.167 M Na_2HPO_4 - 0.083 M NaH_2PO_4 buffer. The extraction process was repeated to ensure complete removal, and the resulting dichloromethane solution was dried by passing it through a 4-mL cartridge of anhydrous Na_2SO_4 . Quantitative elution from the cartridge was effected by flushing it with an additional 5-10 mL of dichloromethane. The purified product was taken to near dryness under a stream of nitrogen and diluted to obtain nominal concentrations of 5 ng/ μl per component when on-column injection techniques were employed or 50 ng/ μl when split/splitless injection was used. Injection volumes were typically 0.2 μl .

Conditions for Gas Chromatography and Mass Spectrometry

All investigations were carried out on a GC-Carlo Erba Model 4662. The sample injection techniques were split/splitless and on-column. Helium was used as the carrier gas (1 mL/min).

The MS interface temperature was 300° C. The GC was directly interfaced to a Kratos MS-80 magnetic mass spectrometer with a Data General Nova 4-based DS-55 data system. MS conditions were: EI ionizing voltage, 70 eV; dynamic MS resolution, 1000; scan rate, 0.5 sec/decade; source pressure, 5×10^{-6} torr; and source temperature, 300° C.

Separations were compared on three different capillary columns:

1. 100 m x 0.25 mm ID, 0.5 μm film thickness, 007-series methylsilicone bonded-phase fused-silica column, Quadrex Corp., New Haven, CT.
2. 30 m x 0.25 mm ID, 0.25 μm film thickness, DB-5 95% dimethyl-5%-diphenyl-polysiloxane bonded-phase fused-silica column, J&W Scientific, Folsom, CA.
3. 30 m x 0.25 mm ID, 0.25 μm film thickness, DB-210 methyl-3,3,3-trifluoropropyl-polysiloxane bonded-phase fused silica column, J&W Scientific, Folsom, CA.

The respective column conditions are shown in table 1.

TABLE 1. - Conditions for GC columns

Column	Column head pressure	Injection technique	Temp. for injector	Temperature Program		Final temp.
				Initial temp. and duration	Rate	
DB-5	0.7 Kg/cm ²	split/splitless	300° C	20° C initial (2-min hold)	20° C/min to 70° C, then 2° C/min to 250° C	250° C
	0.7 Kg/cm ²	on column	50° C	50° C initial (2-min hold)	8° C/min to 70° C, then 2° C/min to 250° C	250° C
DB-210	0.7 Kg/cm ²	split/splitless	300° C	20° C initial (2-min hold)	20° C/min to 70° C, then 2° C/min to 240° C	240° C
	0.7 Kg/cm ²	on column	50° C	50° C initial (2-min hold)	8° C/min to 70° C, then 2° C/min to 240° C	240° C
Methyl-silicone	2.8 Kg/cm ²	split/splitless	300° C	20° C initial (2-min hold)	20° C/min to 70° C, then 2° C/min to 320° C	320° C
	2.8 Kg/cm ²	on column	50° C	50° C initial (2-min hold)	8° C/min to 70° C, then 2° C/min to 320° C	320° C

Determination of Retention Indices and Relative Response Factors

The retention indices were calculated using acylated 4-fluorophenol (phenol was used in early work) and 1-naphthol or 1-naphthol and 9-phenanthrol as reference compounds as follows:

$$RI = 100 \times \left[1 + \frac{t_{R(x)} - t_{R(4\text{-fluorophenol})}}{t_{R(1\text{-naphthol})} - t_{R(4\text{-fluorophenol})}} \right]$$

$$RI = 100 \times \left[2 + \frac{t_{R(x)} - t_{R(1\text{-naphthol})}}{t_{R(9\text{-phenanthrol})} - t_{R(1\text{-naphthol})}} \right]$$

The above relation is analogous to that used by White and Li (1) for underivatized phenols which was, in turn, based on the work of Van Den Dool and Kratz (2). T_R is retention time, and $t_{R(x)}$ is the retention time of a given acylated phenolic compound.

Relative response factors were calculated as follows:

$$RF = (A_x/A_s) + (W_s/W_x),$$

where A = area or area percent, and W = weight or weight percent
x = unknown, and s = standard (4-fluorophenol).

SECTION I

COMPARISON OF GC RETENTION INDICES AND MASS SPECTRA OF ACYLATED VERSUS UNDERIVATIZED PHENOLIC COMPOUNDS

GC retention indices for underivatized and derivatized (C_0 - C_2)-phenol (phenol, methylphenol and dimethyl/ethylphenol) isomers on the DB-5 and methylsilicone columns are shown in table 2. Three pairs of the underivatized isomers coelute from the DB-5 column: m- and p-methylphenol, 2,5- and 2,4-dimethylphenol, p-ethylphenol and 3,5-dimethylphenol. Also, two underivatized isomeric pairs coelute from the methylsilicone column: m- and p-methylphenol, and 3,5-dimethylphenol and 3-ethylphenol. All derivatized (C_0 - C_2)-phenols separate on the methylsilicone column, while 2,3-dimethylphenol and p-ethylphenol esters coelute from the DB-5 column.

Figure 1 compares chromatograms obtained for underivatized versus derivatized (C_0 - C_2)-phenols on the methylsilicone column. The improved peak shape and overall degree of resolution obtained after acylation is obvious. The generality of the above finding is dramatically illustrated by figure 2, which contrasts chromatograms of an ArOH-enriched fraction from a commercial jet fuel with and without prior acylation. The significantly lower elution temperature required for the derivatized ArOH is also apparent in the figure.

Comparisons of spectra for underivatized versus derivatized phenols are shown in figures 3-5. The underivatized benzyl alcohol, o-cresol, m-cresol, and p-cresol all exhibit significant peaks at m/z 108, 107, 91, 90, 79, and 77. Of the four compounds, only benzyl alcohol can be readily differentiated because of its intense peaks at m/z 77 and 79. On the other hand, spectra of all the corresponding derivatives are easily distinguished. For example, the base peak for derivatized o-cresol occurs at m/z 107, and at m/z 204 for derivatized m-cresol and p-cresol; the latter may be recognized by distinctly different intensities at m/z 107 and 91, for example. The spectrum of benzyl alcohol shows significant differences from those of the C_1 -phenols; for example, it does not exhibit an (M-29) ion, (m/z 175) corresponding to loss of CHO.

TABLE 2. - Retention indices of underivatized and derivatized (C₀-C₂)-phenols

Compound No.	Chemical name	GC Retention Index*			
		DB-5		Methylsilicone	
		Under.	Der.	Under.	Der.
	Isopropylbenzene (cumene)	94.22	107.01	-	-
1	Phenol	100	100	100	100
3	2-Methylphenol	110.66	109.14	114.08	114.02
4	3-Methylphenol	114.17	112.85	118.02	118.66
5	4-Methylphenol	114.17	114.08	118.02	120.35
6	2,6-Dimethylphenol	119.64	120.72	124.73	129.39
12	2-Ethylphenol	125.23	121.35	130.28	129.72
7	2,5-Dimethylphenol	127.50	125.60	132.97	134.46
8	2,4-Dimethylphenol	127.50	126.95	132.56	136.01
13	3-Ethylphenol	130.69	128.36	136.49	137.12
14	4-Ethylphenol	131.40	131.52	136.00	140.74
9	3,5-Dimethylphenol	131.40	130.52	136.49	139.39
10	2,3-Dimethylphenol	132.90	131.52	138.44	141.13
11	3,4-Dimethylphenol	135.96	137.73	141.30	146.79
75	1-Naphthol	200	200	200	200

*RI based on phenol and 1-naphthol.

The underivatized 2-ethylphenol, 2,4-dimethylphenol, and 3,5-dimethylphenol (figure 4) all show prominent molecular ions (M⁺, m/z 122), M-1, and M-15 ions. The two dimethylphenol spectra are virtually identical while the 2-ethylphenol spectrum may be recognized by its lower molecular ion abundance. Once again, the spectra from derivatized C₂-phenols are much more characteristic of each compound. For example, the spectrum for derivatized 2-ethylphenol shows a prominent peak at m/z 203 (M-15), which is characteristic of ethyl versus dimethyl substitution. Base peaks for 2,4-dimethylphenol and 3,5-dimethylphenol are m/z 121 (M-97) and m/z 218 (M⁺), respectively. A prominent M-97 fragment is characteristic of all *o*-alkylphenols; this feature is also evident in the spectra of *o*-cresol and *o*-ethylphenol derivatives.

Underivatized 2,3,6-trimethylphenol, 4-isopropylphenol, and 3-ethyl-5-methylphenol (figure 5) all exhibit similar spectra with base peaks at m/z 121; m/z 136 (M⁺) is the second most abundant peak. The spectrum of 2-*n*-propylphenol differs from those of the other C₃-phenols in that its base peak occurs at m/z 107. As expected, the corresponding spectra for derivatized

FIGURE 1. - GC/MS total ion current (TIC) chromatograms of underivatized (A) and derivatized (B) (C_0 - C_2)-phenols on the methylsilicone column (see table 2).

FIGURE 2. - GC/MS total ion current (TIC) chromatograms of an ArOH concentrate obtained from a JP-5 jet fuel before (A) and after (B) derivatization.

FIGURE 3. - Mass spectra of underivatized and derivatized C_7H_8O compounds.

FIGURE 4. - Mass spectra of underivatized and derivatized C₂-phenolic compounds.

FIGURE 5. - Mass spectra of underivatized and derivatized C_3 -phenolic compounds.

C₃-phenols are markedly different from one another. Although the base peaks for derivatized 4-isopropylphenol as well as 3-ethyl-5-methylphenol occur at m/z 217 (M-15), they are easily differentiated by the prominent 103 ion in the spectrum of 4-isopropylphenol. The base peak at m/z 203 is characteristic of n-propyl as opposed to other C₃-substitution patterns. The minimal intensity of the M-15 fragment ion (m/z 217) as well as the prominent ion at m/z 135 (M-97) for 2,3,6-trimethylphenol are consistent with its trimethyl--as opposed to propyl- or methyl-ethyl-substitution pattern and the fact that it contains o-substituents.

In general, mass spectra of acylated hydroxyl compounds are much more characteristic both in the sense of specific compound identification as well as being able to deduce structural features of an unknown compound from its spectrum. Addition of the trifluoroacetyl group significantly alters the fragmentation mechanism of the parent compound, in addition to providing the opportunity for hydrogen-fluorine exchange and for formation of fragments which are not possible in the case of underivatized species.

SECTION II

COMPARISON OF GC RESOLUTION OF ACYLATED ArOH USING DIFFERENT COLUMNS

(C₀-C₃)-phenolic compounds were acylated and analyzed on three capillary columns, DB-5, DB-210, and methylsilicone. The retention indices are shown in table 3. As noted earlier in Section I, the DB-5 column cannot resolve *p*-ethylphenol and 2,3-dimethylphenol; those compounds were resolved on the DB-210 and methylsilicone columns. For this reason, only the latter two columns underwent more extensive evaluation.

GC/MS chromatograms of (C₀-C₂)- and C₃-phenol derivatives on DB-210 and methylsilicone columns are shown in figures 6 and 7, respectively. DB-210 separates (C₀-C₂)-phenols to a greater degree than methylsilicone but provides only marginal resolution of 4-isopropylphenol/2,3,6-trimethylphenol and 2,4,5-trimethylphenol/2,3,5-trimethylphenol. The methylsilicone column adequately resolves all the C₃-phenols.

Figure 8 shows GC/MS chromatograms of an acylated acid fraction isolated from an SRC-II 200-325° C coal liquid distillate using nonaqueous ion exchange chromatography. The number of peaks evident in the chromatogram obtained using the methylsilicone column is at least three times more than the DB-210 column. In the authors' experience, the methylsilicone column significantly outperformed the DB-210 column in its ability to resolve and elute higher molecular weight ArOH derivatives. It also outperformed the DB-5 column. Although not a rigorous test, the consistently higher degree of resolution of actual ArOH fractions obtained with methylsilicone columns, coupled with their widespread applicability toward other types of analyses, has led to their exclusive use in current applications.

TABLE 3. - Retention indices for (C₀-C₃)-acylated phenols
on DB-5, DB-210, and methylsilicone columns

Compound No.	Compound Name	GC Retention Index*					
		Methyl- silicone	S ¹	DB-5	S	DB-210	S
	Isopropylbenzene	112.72	0.03	107.01	0.02	91.12	0.05
64	p-Fluorophenol	98.42	0.03	NA	NA	102.28	0.06
1	Phenol	100	-	100	-	100	-
3	o-Methylphenol	114.05	0.03	109.14	0.03	107.26	0.03
4	m-Methylphenol	118.67	0.01	112.85	0.05	111.49	0.03
5	p-Methylphenol	120.33	0.03	114.08	0.01	112.51	0.06
6	2,6-Dimethylphenol	129.34	0.03	120.72	0.06	114.43	0.06
12	o-Ethylphenol	129.73	0.01	121.35	0.02	115.40	0.08
7	2,5-Dimethylphenol	134.41	0.03	125.60	0.06	120.26	0.05
8	2,4-Dimethylphenol	135.95	0.06	126.95	0.02	122.06	0.10
13	m-Ethylphenol	137.01	0.09	128.36	0.04	123.26	0.13
14	p-Ethylphenol	140.60	0.07	131.52	0.06	125.62	0.07
9	3,5-Dimethylphenol	139.37	0.03	130.52	0.04	126.31	0.09
10	2,3-Dimethylphenol	141.06	0.09	131.52	0.06	127.88	0.12
11	3,4-Dimethylphenol	146.71	0.06	137.73	0.05	133.83	0.10
15	2-Isopropylphenol	139.91	0.16	130.16	NA	120.62	0.16
18	2-n-Propylphenol	147.47	0.18	137.54	NA	127.04	0.18
20	2,4,6-Trimethylphenol	151.90	0.15	141.84	NA	130.40	0.23
16	3-Isopropylphenol	148.79	0.21	139.43	NA	131.36	0.16
17	4-Isopropylphenol	154.16	0.19	144.76	NA	135.76	0.25
21	2,3,6-Trimethylphenol	157.30	0.32	147.60	NA	136.18	0.19
19	4-n-Propylphenol	160.31	0.13	151.72	NA	141.38	0.22
22	2,3,5-Trimethylphenol	162.00	0.28	153.44	NA	144.21	0.06
23	2,4,5-Trimethylphenol	162.92	0.20	154.30	NA	144.94	0.11
24	3,4,5-Trimethylphenol	174.20	0.40	168.21	NA	160.16	0.19
75	1-Naphthol	200	-	200	-	200	-

*RI. based on phenol and 1-naphthol.

¹ S = standard deviation.

² NA = not available.

FIGURE 6. - GC/MS chromatograms of acylated (C_0 - C_2)-phenols on DB-210 (A) and methylsilicone (B) columns. Peaks are identified in table 3.

FIGURE 7. - GC/MS chromatograms of acylated C₃-phenols on DB-210 (A) and methylsilicone (B) columns. Peaks are identified in table 3.

FIGURE 8. - GC/MS chromatograms of an acylated acid concentrate from SRC-II 200°-325° C distillate on DB-210 and methylsilicone columns.

SECTION III

COMPARISON WITH LIBRARY SPECTRA

A comparison of mass spectra obtained in this study with those supplied in the Kratos DS-55 library is shown in table 4. Presumably, the library spectra are taken from the work of Saxby (3). Comparison of individual spectra obtained over the course of this work indicates relative repeatabilities (relative standard deviations) of ± 10 percent for ions with intensities ≥ 30 percent of the base peak. However, it is recognized that interlaboratory comparisons of spectra typically show greater differences due to systematic variations stemming from differences in instrument design and operation. Thus, the main value in comparing the library data with our data is to enable the reader to assess the potential for variation between spectra shown here versus those obtainable on his instrument.

In general, the two sets of data agree within 20 percent (relative) for most ions. The 20 percent figure is approximately consistent with a ± 10 percent random variation in intensity from either instrument. Interestingly, corresponding spectra from *o*-alkylphenol derivatives generally show significantly better agreement than those for non-*o*-phenols; the agreement in ion intensities corresponding to loss of $\text{CF}_3\text{C}(\text{O})\text{O}$ (M-113) is especially poor for *m*- and *p*-isomers. In addition, CF_3^+ ion intensities (m/z 69) for derivatives of phenol and 3-methylphenol are in poor agreement. Overall, however, the spectra agree well enough to obtain correct qualitative identifications using either data set.

Perhaps the most significant observation from the above comparison is that reference spectra for only eight relatively simple alkylphenol trifluoroacetate esters are available in current libraries.

TABLE 4. - Comparison of intensity (percent base peak) of important ions for trifluoroacetate esters with those in the MS library

Compound	M+	M-CH ₃	M-CO	M-HCO	M-CO-CH ₃	M-CF ₃	M-COCF ₃	M-OCOCF ₃	M-HOCOCF ₃	M-COCF ₃ -CO	C ₇ H ₆ ⁺	C ₇ H ₇ ⁺	C ₆ H ₅ ⁺	CF ₃ ⁺
Phenol	(1) 100 (2) 100		43 44			6 6	41 27	62 44	3 -	122 92			62 44	83 56
2-Methylphenol	(1) 57 (2) 64		1 -	8 12		5 7	100 100	48 56	55 48	28 -	10 10	48 56	55 56	38 32
3-Methylphenol	(1) 113 (2) 88	2 -	9 7	40 28		6 -	31 24	100 100	66 28	47 36	18 11	100 100	56 40	64 36
4-Methylphenol	(1) 100 (2) 100	0 -	6 -	29 28		2 -	76 56	56 40	72 38	56 44	10 7	56 40	72 48	50 60
2-Ethylphenol	(1) 41 (2) 36	36 -			4 -	10 -	100 100	34 48	57 56	6 10	54 40	26 32	45 48	39 32
3,4-Dimethylphenol	(1) 100 (2) 100	10 -	1 -	6 -	22 21	1 -	69 68	31 30	78 40	29 30	8 -	45 40	61 52	39 40
2,6-Dimethylphenol	(1) 57 (2) 60	2 -		1 -	3 -	3 -	100 100	39 44	46 40	13 11	4 -	43 40	53 44	25 22
2,4-Dimethylphenol	(1) 47 (2) 56	1 -		2 -	4 4	2 -	100 100	18 22	26 18	13 10	2 -	30 32	39 27	20 15

(1) Present work.

(2) Data from library search. Dash (-) indicates no entry in the library.

SECTION IV

SPECTRA, RETENTION INDICES, AND RELATIVE RESPONSE FACTORS FOR ACYLATED PHENOLIC COMPOUNDS

Table 5 lists the compounds investigated along with their retention indices on the methylsilicone column and their total ion current (TIC) responses relative to that of 4-fluorophenol. It should be noted, however, that all data apply to fully acylated (i.e., in the case of multiple hydroxyl compounds) species. Compounds are listed according to their empirical formula: $C_nH_{2n+Z}OX$. Within a given series (value of Z), the compounds are listed in order of increasing n. Compounds with elements (X) in addition to CHO are arranged in alphabetical order of X. The various Z-series are listed according to increasingly negative values of Z.

Retention indices typically were reproducible within one or two parts per thousand. The relative precision of response factors normally ranged from 10 to 20 percent. In general, precision was limited by the instruments used and not the chemical derivatization procedure itself. For example, variations in results from multiple injection of a single derivatized sample were equal to those from single injections of replicate derivatized samples. The principle limiting factor on precision is probably the GC injection technique. Also, had standard addition or multiple internal standard techniques been employed, precision of response factors with the existing instrumental configuration probably would have been improved. Mass spectra corresponding to compounds in table 5 are reproduced elsewhere (8).

TIC response factors in table 5 were obtained using cool on-column injection because significant degradation was noted for selected compounds introduced via the heated split/splitless inlet. For example, acylated cyclic benzylic alcohols (e.g., 1,2,3,4-tetrahydro-1-naphthol, 1-acenaphthenol, and 1-indanol) were converted to the corresponding alkene:

Based on peak areas, up to 50 percent formation of alkenes was observed. In addition, during analysis of lower alkylphenols, enhanced relative peak areas for o-substituted compounds, presumably due to degradation of m- and p-substituted species, were occasionally noted with split/splitless injection. For these reasons, the on-column technique is preferred for quantitative analysis.

Given the above, no systematic variation in TIC response with structure was observed. Although response was corrected for purity, where possible, the presence of nonvolatile impurities or other unknown factors could cause negative errors in TIC data. In cases where purity was in doubt or could not be reasonably estimated, e.g., components in actual samples, TIC response was not calculated. On the other hand, correlation of retention index with structure appears feasible and will be reported in detail later.

A number of characteristic or unusual fragmentation pathways, not noted by Saxby (3) in his earlier study, are evident in the accompanying mass spectra. A detailed discussion of these is beyond the scope of this volume and will be reported separately. However, selected spectral features of alkylphenol derivatives are noted below as examples.

Alkylphenols with normal alkyl (C_n , $n > 1$) substituents show significant fragmentation from benzylic side chain cleavage of the longest substituent evidenced by a major peak at m/z ($M - C_{n-1}H_{2(n-1)+1}$). In addition, hydrogen transfer to the aromatic ring (McLafferty rearrangement) was observed in ortho and meta normal alkyl (C_n , $n \geq 4$) phenol esters, but was more prominent in meta isomers. This effect is recognizable by the appearance of a significant peak at m/z 204, corresponding to the loss of $C_{n-1}H_{2(n-1)}$ mass units from the molecular ion. The m/z 204 ion is typically the base peak for m-n-alkyl (C_n , $n \geq 4$) trifluoroacetates; its lower abundance in spectra of o-n-alkyl trifluoroacetates is consistent with the 50 percent lower probability of the hydrogen transfer in ortho versus meta isomers. A prominent m/z 204 ion (McLafferty arrangement) was never observed in spectra of p-n-alkyl isomers. Similar effects have been observed by Rullkotter et al. (9) for alkylthiophenes.

Compounds with two identical branched alkyl (C_n) substituents exhibit prominent fragment ions corresponding to the substituent, C_nH_{2n+1} . For example, 2,4-di-tert-butylphenol and 2,6-di-sec-butylphenol exhibit base peaks at m/e 57 (C_4H_9), 2,5-diisopropylphenol and 2,6-diisopropylphenol exhibit base peaks at m/e 43 (C_3H_7), and 2,4-di-sec-butylphenol exhibits a peak at m/z 57 (C_4H_9) as its next-to-most abundant peak.

In addition, fragment ions resulting from loss of CH_2F (m/z 33) are observed in compounds containing a branched alkyl group ortho to the trifluoroacetyl moiety. A fluorine-hydrogen exchange, a relatively rare phenomenon, must occur in these cases.

TABLE 5. - GC retention indices and MS response factors of acylated phenolic compounds

No.	Chemical name	Z-series	Empirical formula $C_nH_{2n+2}O$	Molecular weight (unreacted)	Molecular weight (reacted)	GC retention index ¹		Relative response factor ²	
						RI	S ³	TIC	S ³
1	phenol	-6(0)	C ₆ H ₆ O	94	190	101.31	0.06	0.97	0.11
2	benzyl alcohol	-6(0)	C ₇ H ₈ O	108	204	127.28	0.03	1.02	0.19
3	o-cresol	-6(0)	C ₇ H ₈ O	108	204	115.9	0.08	1.34	0.08
4	m-cresol	-6(0)	C ₇ H ₈ O	108	204	119.74	0.12	1.26	0.12
5	p-cresol	-6(0)	C ₇ H ₈ O	108	204	120.89	0.40	1.00	0.11
6	2,3-dimethylphenol	-6(0)	C ₈ H ₁₀ O	122	218	141.64	0.47	1.29	0.25
7	2,4-dimethylphenol	-6(0)	C ₈ H ₁₀ O	122	218	136.71	0.30	1.31	0.27
8	2,5-dimethylphenol	-6(0)	C ₈ H ₁₀ O	122	218	135.20	0.28	1.38	0.20
9	2,6-dimethylphenol	-6(0)	C ₈ H ₁₀ O	122	218	130.20	0.28	1.38	0.06
10	3,4-dimethylphenol	-6(0)	C ₈ H ₁₀ O	122	218	147.28	0.39	1.35	0.26
11	3,5-dimethylphenol	-6(0)	C ₈ H ₁₀ O	122	218	139.98	0.40	1.44	0.27
12	2-ethylphenol	-6(0)	C ₈ H ₁₀ O	122	218	130.57	0.23	1.43	0.29
13	3-ethylphenol	-6(0)	C ₈ H ₁₀ O	122	218	137.76	0.37	1.28	0.37
14	4-ethylphenol	-6(0)	C ₈ H ₁₀ O	122	218	140.80	0.25	1.12	0.12
15	2-isopropylphenol	-6(0)	C ₉ H ₁₂ O	136	232	139.91	0.16	1.21	0.15
16	3-isopropylphenol	-6(0)	C ₉ H ₁₂ O	136	232	148.79	0.21	0.90	0.04
17	4-isopropylphenol	-6(0)	C ₉ H ₁₂ O	136	232	154.16	0.19	1.61	0.00
18	2-n-propylphenol	-6(0)	C ₉ H ₁₂ O	136	232	147.47	0.18	1.06	0.02
19	3-n-propylphenol*	-6(0)	C ₉ H ₁₂ O	136	232	156.35	0.06	-	-
20	4-n-propylphenol	-6(0)	C ₉ H ₁₂ O	136	232	160.31	0.13	1.00	0.15
21	2,3,5-trimethylphenol	-6(0)	C ₉ H ₁₂ O	136	232	162.00	0.28	1.29	0.00
22	2,3,6-trimethylphenol	-6(0)	C ₉ H ₁₂ O	136	232	157.30	0.32	1.19	0.10
23	2,4,5-trimethylphenol	-6(0)	C ₉ H ₁₂ O	136	232	162.92	0.20	1.33	0.07
24	2,4,6-trimethylphenol	-6(0)	C ₉ H ₁₂ O	136	232	151.90	0.15	1.28	0.02
25	3,4,5-trimethylphenol	-6(0)	C ₉ H ₁₂ O	136	232	173.20	0.14	1.26	0.04
26	2,6-diethylphenol	-6(0)	C ₁₀ H ₁₄ O	150	246	161.99	0.01	1.45	0.16
27	3,4-dimethyl-6-ethylphenol	-6(0)	C ₁₀ H ₁₄ O	150	246	177.36	0.13	1.58	0.05
28	3-n-butylphenol*	-6(0)	C ₁₀ H ₁₄ O	150	246	177.17	- ⁴	-	-
29	4-n-butylphenol	-6(0)	C ₁₀ H ₁₄ O	150	246	181.77	0.31	1.09	0.13
30	2-sec-butylphenol	-6(0)	C ₁₀ H ₁₄ O	150	246	156.50	0.53	1.38	0.23
31	4-sec-butylphenol	-6(0)	C ₁₀ H ₁₄ O	150	246	172.40	0.33	0.98	0.21
32	2-tert-butylphenol	-6(0)	C ₁₀ H ₁₄ O	150	246	160.12	0.16	1.07	0.06
33	4-tert-butylphenol	-6(0)	C ₁₀ H ₁₄ O	150	246	168.38	0.03	1.51	0.07

See footnotes at end of table.

TABLE 5. - GC retention indices and MS response factors of acylated phenolic compounds--Continued

No.	Chemical name	Z-series	Empirical formula	Molecular weight	Molecular weight	GC retention index ¹		Relative response factor ²	
			C _n H _{2n+2} O	(unreacted)	(reacted)	RI	S ³	TIC	S ³
34	2-isopropyl-5-methylphenol	-6(0)	C ₁₀ H ₁₄ O	150	246	160.01	0.40	1.58	0.42
35	4-isopropyl-3-methylphenol	-6(0)	C ₁₀ H ₁₄ O	150	246	177.78	0.08	1.22	0.04
36	5-isopropyl-2-methylphenol	-6(0)	C ₁₀ H ₁₄ O	150	246	163.68	0.46	1.06	0.15
37	5-isopropyl-3-methylphenol	-6(0)	C ₁₀ H ₁₄ O	150	246	168.17	0.45	1.60	0.31
38	2-methyl-6-n-propylphenol	-6(0)	C ₁₀ H ₁₄ O	150	246	163.24	0.21	1.44	0.08
39	2-tert-butyl-4-methylphenol	-6(0)	C ₁₁ H ₁₆ O	164	260	180.44	0.22	1.17	0.18
40	2-tert-butyl-6-methylphenol	-6(0)	C ₁₁ H ₁₆ O	164	260	177.45	0.13	1.45	0.23
41	2-(3-methylbutyl)phenol	-6(0)	C ₁₁ H ₁₆ O	164	260	176.99	0.36	1.42	0.22
42	3-n-pentylphenol*	-6(0)	C ₁₁ H ₁₆ O	164	260	196.50	0.31	-	-
43	4-n-pentylphenol	-6(0)	C ₁₁ H ₁₆ O	164	260	202.37	0.06	1.26	0.05
44	4-tert-pentylphenol	-6(0)	C ₁₁ H ₁₆ O	164	260	189.92	0.23	1.37	0.27
45	2,5-diisopropylphenol	-6(0)	C ₁₂ H ₁₈ O	178	274	186.47	0.23	1.59	0.28
46	2,6-diisopropylphenol	-6(0)	C ₁₂ H ₁₈ O	178	274	176.93	0.13	1.15	0.05
47	6-tert-butyl-2,4-dimethylphenol	-6(0)	C ₁₂ H ₁₈ O	178	274	196.18	0.24	1.37	0.13
48	3-n-hexylphenol*	-6(0)	C ₁₂ H ₁₈ O	178	274	215.86	0.13	-	-
49	4-n-hexylphenol	-6(0)	C ₁₂ H ₁₈ O	178	274	221.69	0.25	1.26	0.19
50	3-n-heptylphenol*	-6(0)	C ₁₃ H ₂₀ O	192	288	233.84	0.13	-	-
51	2,4-di-sec-butylphenol	-6(0)	C ₁₄ H ₂₂ O	206	302	215.09	0.57	1.95	0.21
52	2,4-di-tert-butylphenol	-6(0)	C ₁₄ H ₂₂ O	206	302	212.81	0.11	1.28	0.07
53	2,6-di-sec-butylphenol	-6(0)	C ₁₄ H ₂₂ O	206	302	205.87	0.30	1.62	0.26
54	3-n-octylphenol*	-6(0)	C ₁₄ H ₂₂ O	206	302	251.03	- ⁴	-	-
55	4-n-octylphenol	-6(0)	C ₁₄ H ₂₂ O	206	302	258.00	0.40	1.38	0.28
56	3-n-nonylphenol*	-6(0)	C ₁₅ H ₂₄ O	220	316	267.36	- ⁴	-	-
57	4-n-decylphenol	-6(0)	C ₁₆ H ₂₆ O	234	330	292.22	0.46	1.33	0.14
58	2,4-dimethyl-6(2,4,4-tri- methylpentyl)phenol	-6(0)	C ₁₆ H ₂₆ O	234	330	242.11	0.45	2.04	0.01
59	3-n-undecylphenol*	-6(0)	C ₁₇ H ₂₈ O	248	344	297.84	- ⁴	-	-
60	2-n-dodecylphenol	-6(0)	C ₁₈ H ₃₀ O	262	358	315.51	0.36	2.49	0.56
61	4-n-dodecylphenol	-6(0)	C ₁₈ H ₃₀ O	262	358	324.14	0.51	1.34	0.14
62	3-n-pentadecylphenol	-6(0)	C ₂₁ H ₃₆ O	304	400	366.27	3.30	1.60	0.37
63	3-fluorophenol	-6(0)	C ₆ H ₅ FO	112	208	97.93	0.06	0.65	0.06
64	4-fluorophenol	-6(0)	C ₆ H ₅ FO	112	208	100.00	- ⁵	1.00	- ⁵

See footnotes at end of table.

TABLE 5. - GC retention indices and MS response factors of acylated phenolic compounds--Continued

No.	Chemical name	Z-series	Empirical formula $C_nH_{2n+2}O$	Molecular weight (unreacted)	Molecular weight (reacted)	GC retention index ¹		Relative response factor ²	
						RI	S ³	TIC	S ³
65	4-(methylthio)phenol	-6(0)	C_7H_8OS	140	236	183.87	0.28	1.15	0.18
66	3-methyl-4-(methylthio)phenol	-6(0)	$C_8H_{10}OS$	154	250	203.57	0.13	1.17	0.15
67	1-indanol	-8(0)	$C_9H_{10}O$	134	230	170.94	- ⁴	0.72	-
68	2-indanol	-8(0)	$C_9H_{10}O$	134	230	174.90	- ⁴	1.00	-
69	4-indanol*	-8(0)	$C_9H_{10}O$	134	230	170.10	- ⁴	-	-
70	5-indanol	-8(0)	$C_9H_{10}O$	134	230	179.22	- ⁴	1.11	-
71	1-hydroxy-1,2,3,4-tetrahydro- naphthalene	-8(0)	$C_{10}H_{12}O$	148	244	194.47	- ⁴	0.76	-
72	5,6,7,8-tetrahydro-1-naphthol	-8(0)	$C_{10}H_{12}O$	148	244	196.28	- ⁴	0.92	-
73	5,6,7,8-tetrahydro-2-naphthol	-8(0)	$C_{10}H_{12}O$	148	244	204.64	- ⁴	1.04	-
74	2-cyclohexylphenol	-8(0)	$C_{12}H_{16}O$	176	272	215.07	- ⁴	1.02	-
75	1-naphthol	-12(0)	$C_{10}H_8O$	144	240	200.00	- ⁶	1.15	0.07
76	2-naphthol	-12(0)	$C_{10}H_8O$	144	240	205.17	0.33	1.44	0.04
77	1-methyl-2-naphthol	-12(0)	$C_{11}H_{10}O$	158	254	224.80	0.23	1.04	0.01
78	2-methyl-1-naphthol	-12(0)	$C_{11}H_{10}O$	158	254	214.66	0.18	1.04	0.07
79	1-naphthalenemethanol	-12(0)	$C_{11}H_{10}O$	158	254	229.40	0.08	1.30	0.06
80	1-naphthaleneethanol	-12(0)	$C_{12}H_{12}O$	172	268	249.77	0.03	1.48	0.04
81	1-acenaphthenol	-14(0)	$C_{12}H_{10}O$	170	266	247.55	0.27	0.75	- ⁴
82	2-phenylphenol	-14(0)	$C_{12}H_{10}O$	170	266	214.62	0.20	1.19	- ⁴
83	3-phenylphenol	-14(0)	$C_{12}H_{10}O$	170	266	237.47	0.33	1.08	- ⁴
84	4-phenylphenol	-14(0)	$C_{12}H_{10}O$	170	266	241.23	0.35	1.57	- ⁴
85	2-benzylphenol	-14(0)	$C_{13}H_{12}O$	184	280	236.48	0.38	1.21	- ⁴
86	4-benzylphenol	-14(0)	$C_{13}H_{12}O$	184	280	251.40	0.43	1.30	- ⁴
87	2-methyl-6-phenylphenol*	-14(0)	$C_{13}H_{12}O$	184	280	129.04	-	-	-
88	2-hydroxy-5,6,7,8-tetrahydro- phenanthrene	-14(0)	$C_{14}H_{14}O$	198	294	305.48	0.54	1.13	- ⁴
89	4-hydroxy-1,2,3,4-tetrahydro- phenanthrene	-14(0)	$C_{14}H_{14}O$	198	294	281.63	0.70	1.17	- ⁴
90	1-hydroxyfluorene	-16(0)	$C_{13}H_{10}O$	182	278	268.02	0.01	1.13	0.24
91	2-hydroxyfluorene	-16(0)	$C_{13}H_{10}O$	182	278	278.67	0.64	1.19	0.20
92	3-hydroxyfluorene	-16(0)	$C_{13}H_{10}O$	182	278	277.50	0.30	0.97	0.26

See footnotes at end of table.

TABLE 5. - GC retention indices and MS response factors of acylated phenolic compounds--Continued

No.	Chemical name	Z-series	Empirical formula $C_nH_{2n+Z}O$	Molecular weight (unreacted)	Molecular weight (reacted)	GC retention index ¹		Relative response factor ²	
						RI	S ³	TIC	S ³
93	4-hydroxyfluorene	-16(0)	$C_{13}H_{10}O$	182	278	271.65	0.22	2.38 ⁷	0.16
94	9-hydroxyfluorene	-16(0)	$C_{13}H_{10}O$	182	278	257.45	0.06	1.00	0.07
95	2-fluorenomethanol	-16(0)	$C_{14}H_{12}O$	196	292	302.90	0.54	0.80	0.25
96	9-phenanthrol	-18(0)	$C_{14}H_{10}O$	194	290	300	- ₆	- ₇	-
97	1,2-dihydroxybenzene	-6(0 ₂)	$C_6H_6O_2$	110	206	126.85	0.55	1.00	0.19
98	1,3-dihydroxybenzene	-6(0 ₂)	$C_6H_6O_2$	110	206	131.21	0.18	1.20	0.28
99	1,4-dihydroxybenzene	-6(0 ₂)	$C_6H_6O_2$	110	206	133.69	0.73	1.44	0.23
100	2,3-dihydroxytoluene	-6(0 ₂)	$C_7H_8O_2$	124	220	141.33	0.21	0.39 ⁷	0.16
101	2,5-dihydroxytoluene	-6(0 ₂)	$C_7H_8O_2$	124	220	147.25	0.65	1.45	0.12
102	2,6-dihydroxytoluene	-6(0 ₂)	$C_7H_8O_2$	124	220	140.96	0.00	1.12	0.01
103	3,4-dihydroxytoluene	-6(0 ₂)	$C_7H_8O_2$	124	220	147.39	0.11	0.55 ⁷	0.11
104	3,5-dihydroxytoluene	-6(0 ₂)	$C_7H_8O_2$	124	220	149.22	0.26	1.09	0.09
105	2-methoxyphenol	-6(0 ₂)	$C_7H_8O_2$	124	220	141.00	0.59	1.17	0.11
106	2-ethoxyphenol	-6(0 ₂)	$C_8H_{10}O_2$	138	234	153.77	0.55	1.36	0.28
107	2,4-dihydroxyethylbenzene	-6(0 ₂)	$C_8H_{10}O_2$	138	234	161.31	0.04	1.22	0.31
108	1,3-dihydroxy-n-pentylbenzene	-6(0 ₂)	$C_{11}H_{16}O_2$	180	276	213.91	0.05	1.12	0.22
109	1,3-dihydroxy-n-hexylbenzene	-6(0 ₂)	$C_{12}H_{18}O_2$	194	290	228.79	0.07	3.89 ⁷	0.15
110	1,3-dihydroxynaphthalene	-12(0 ₂)	$C_{10}H_8O_2$	160	256	219.52	0.43	0.33 ⁷	0.17
111	1,7-dihydroxynaphthalene	-12(0 ₂)	$C_{10}H_8O_2$	160	256	221.93	0.30	0.92	0.26
112	2,7-dihydroxynaphthalene	-12(0 ₂)	$C_{10}H_8O_2$	160	256	234.77	0.03	0.93	0.15
113	2,2'-dihydroxybiphenyl	-14(0 ₂)	$C_{12}H_{10}O_2$	186	282	217.37	0.01	1.13	0.04
114	4,4'-dihydroxybiphenyl	-14(0 ₂)	$C_{12}H_{10}O_2$	186	282	270.42	0.42	1.03	0.20
115	2-hydroxydibenzofuran	-16(0 ₂)	$C_{12}H_8O_2$	184	280	263.92	0.06	1.05	0.12
116	4,5-dihydroxyphenanthrene	-16(0 ₂)	$C_{13}H_{10}O_2$	210	306	292.86	0.26	0.34 ⁷	0.18
117	2-hydroxy-9-fluorenone	-18(0 ₂)	$C_{13}H_8O_2$	196	292	296.62	0.37	0.34 ⁷	0.18
118	2,5-dihydroxyphenanthrene	-18(0 ₂)	$C_{14}H_{10}O_2$	210	306	311.19	1.16	0.69 ⁷	0.06

¹ Methylsilicone column.² Response relative to that of 4-fluorophenol.³ S = standard deviation.⁴ Dash (-) indicates single determination.⁵ Standard for RI and response calculations.⁶ Standard for RI calculation.⁷ Compound was of insufficient purity for reliable determination of response.

*Retention index obtained from actual fuel sample. However, compounds were unequivocally identified through comparisons of GC and MS data with those of related compounds. Because of its unknown concentration in the sample, relative response could not be determined.

REFERENCES

1. White, C. M., and N. C. Li. Anal. Chem., v. 54, 1982, p. 1564.
2. Shulgin, A. T. Anal. Chem., v. 36, 1964, p. 920.
3. Saxby, M. J. Organic Mass Spectrometry, v. 4, 1970, p. 133.
4. Green, J. B., J. S. Thomson, S. K.-T. Yu, C. A. Treese, B. K. Stierwalt, and C. P. Renaudo. Preprints, Div. Fuel Chem., ACS, v. 31, No. 1, 1986, p. 198.
5. Green, J. B., C. A. Treese, S. K.-T. Yu, J. S. Thomson, C. P. Renaudo, and B. K. Stierwalt. Preprints, Div. Fuel Chem., ACS, v. 31, No. 2, 1986, p. 126.
6. Yu, S. K.-T., and J. B. Green. Infrared-Chemical Derivatization Method for Determination of Total Hydroxyls and Carboxyls in Petroleum and Syncrudes. Topical Report NIPER-363, September 1988.
7. Van Den Dool, H., and D. P. Kratz. J. Chromatogr., v. 11, 1963, p. 463.
8. Yu, S. K.-T., R. P. Vrana, and J. B. Green. Retention Indices, Relative Response Factors and Mass Spectra of Trifluoroacetate Esters of Phenolic Compounds Determined by Capillary GC/MS. NIPER Topical Report NIPER-396, January 1989.
9. Rullkotter, J., M. Landraft, and U. Disko. J. of High Resolution Chromatogr. & Chromatogr. Communications, v. 11, 1988, p. 633.

APPENDIX 5

HIGH RESOLUTION MASS SPECTROMETRIC ANALYSIS OF AN HPLC FRACTION CONTAINING DIFUNCTIONAL ACIDS FROM AN SRC-II COAL LIQUID

APPENDIX 5

HIGH RESOLUTION MASS SPECTROMETRIC ANALYSIS OF AN HPLC FRACTION CONTAINING DIFUNCTIONAL ACIDS FROM AN SRC-II COAL LIQUID

by

R. D. Grigsby

ABSTRACT

A strong acids concentrate from an SRC-II >325° C residue was sub-fractionated into compound classes (1)* and the subfraction believed to contain dihydroxyaromatics, subfraction 5, was analyzed by probe micro-distillation/mass spectrometry. The results show that $C_nH_{2n+z}O_2$ compounds are abundant in the subfraction, particularly those with a z number of -14 (dihydroxybiphenyls). By far, the most abundant homolog found was methyl-dihydroxybiphenyl, with the parent and C_2 -homologs being the second and third most abundant species, respectively. Less abundant dioxygen homologs were found in series with z numbers ranging from -16 to -40 over a molecular mass range from 184 to 442 amu.

INTRODUCTION

Probe microdistillation/mass spectrometry (PMD/MS) was developed to analyze mixtures derived from petroleum and other fossil energy sources. The technique has been shown to be useful for analyzing these mixtures as well as others containing components whose volatilities are too low for introduction by conventional gas-chromatographic interface or expansion-volume inlet (2). Unlike GC/MS or LC/MS techniques, PMD/MS does not require the removal of a carrier gas or solvent prior to introduction of the sample components into the ion source of the mass spectrometer. In place of chromatographic separation to aid in component identification, the technique depends instead on partial thermal separation of components and on identification of elemental compositions of the ions by high resolution mass analysis.

*Underlined numbers in parentheses refer to items in the list of references at the end of this appendix.

A specially designed direct-introduction probe is used to introduce the mixtures into a high resolution mass spectrometer. Probe temperature is controlled either linearly or nonlinearly (2) by a programmer, and a maximum linear rate of 200° C/min can be achieved with existing equipment. Most experiments are performed with a programming rate of about 10° C/min, however, because of the limited capability of the mass spectrometer to produce high-resolution spectra at scan rates faster than 10 sec/decade. The nonlinear increase is programmed by feedback of the ion current signal from the mass spectrometer to the programmer. In this mode, the rate of temperature increase is varied to hold the total ion current constant.

EXPERIMENTAL

A Kratos MS-50 high resolution mass spectrometer equipped with a Kratos DS-55 data acquisition system based on a Data General NOVA/4 computer was used to record the spectra. The acids subfraction was introduced with a quartz direct-introduction probe having a temperature range from -150 to +600° C. Probe temperature was controlled linearly with a programmer at 10° C/min over a temperature range from ambient to +600° C. To suppress fragmentation and enhance intensities of the molecular ions, ionization was effected by electron impact at an energy of 10 eV. Seventy scans of the spectrum were recorded at a scan rate of 30 sec/decade and 20,000 resolving power.

DISCUSSION

Six computer programs, named "SPECTR", "READTAP", "PROB", "CHY", "INTCOR", and "ELMCRV" have been developed to process data acquired either at a linearly increasing probe temperature or as a function of time (nonlinear increase in temperature). These programs, written in FORTRAN/77, run sequentially with little manual intervention to convert raw mass/intensity data into qualitative and quantitative results. As many as 100 scans can be processed together. Another program, "XFER" (part of the Data General software) is also required to process the data. All programs except "SPECTR" and "XFER" run on Digital Equipment Corp. PDP 11/70 and MicroVAX-II computers. "SPECTR" and "XFER" execute on the NOVA/4 computer. Program development was undertaken primarily on the PDP 11/70 instead of the NOVA/4 because time on the latter computer is limited by demands for data acquisition from the MS-50 mass spectrometer. With minor modifications, all programs should run on the NOVA/4 or other computer having a FORTRAN compiler.

All programs except "ELMCRV" provide preliminary processing of the data to get it into a format that can serve as input to "ELMCRV". This program then calculates elimination curves for the sample ions, i.e., plots of ion intensity vs. temperature (or time). By using nonlinear regression, the temperature/intensity (or time/intensity) data for each mass and z number, describing each ion, are used to evaluate four parameters A, B, C, and D in the skewed Gaussian equation:

$$I = A.e^{-\left[\frac{T-B}{C-D(T-B)}\right]^2} \quad (1)$$

in which I is the intensity of a sample peak and T the absolute temperature (or time). After they are evaluated, the parameters are used to calculate the maximum intensity of the curve, IMAX, the temperature (or time) at which the maximum occurs, T(IMAX), and the area under the curve, AREA. Ninety percent confidence intervals are included.

Output, consisting of line-printer plots of the curves and other results, is saved in file "ELMCRV.OUT". Given with each curve are the name of the data set, the maximum ppm error, elemental combination, z number, and mass. If the regression analysis is successful, the goodness of fit (R^2), number of the best iteration obtained by minimizing the sum of the squares, maximum number of iterations allowed, values of IMAX, T(IMAX), AREA, and the parameters with ninety percent confidence intervals are included.

Figure 1 illustrates the type of output obtained when the ion current as a function of temperature (or time) is strong. It is evident that the curve is almost Gaussian with slight skewing on the right-hand side. Nearly symmetrical curves are typical for the distillation of abundant components from a complex mixture. On the other hand, distillation of an abundant component from a simple mixture produces a curve skewed to the left with an almost vertical drop of intensity to zero on the right-hand side. The difference in distillation behavior can be ascribed to variations in thermodynamic properties of components in simple vs. complex mixtures, and a detailed explanation is outside the scope of the present discussion. The extent of skewing determines the value of D in equation (1), and it is seen that this parameter is near zero for the data shown in Figure 1.

SRCFR5. 11/26/86. SRC-II >325 DEG C STRONG ACIDS, FRACTION 5 SCANS: 50-120
 MAXIMUM PP* ERROR = 6.0 ELEMENTAL COMPOSITION: C(N)H(2N+2)O(2)
 Z = -14 MASS = 186. GOODNESS OF FIT (R**2) = 0.993 BEST ITERATION NO. = 20 NUMBER ALLOWED = 20
 IMAX/10000 = 148.65 +- 8.78 T(IMAX) = 404.90 +- 0.29 K AREA/10000 = 9213.25 +- 581.34
 A/10000 = 148.66 +- 8.78 B = 404.90 +- 0.29 K C = 34.55 +- 0.75 K D = -0.09 +- 0.02

FIGURE 1. - Elimination curve obtained by the probe microdistillation of $C_{12}H_{10}O_2$, $M = 186$, from acids subfraction No. 5 isolated from the >325° C distillate of an SRC-II coal liquid. Plot of ion current (arbitrary units) vs. temperature in Kelvin.

When an ion has less than the specified minimum number of temperature/intensity (or time/intensity) values, e.g., five, the data are ignored. However, because the input file to program "ELMCRV" contains all of the assignments from all of the scans, the data are not lost. Normally, this file, "ELMCRV.DAT", is printed and saved for reference. If a curve cannot be calculated because low intensities cause excessive data scatter, only the points are plotted. In this case, the temperature (or time) centroid and area obtained by adding the areas of trapezoids are calculated and given along with the minimum allowed value of R^2 , the maximum intensity, and the corresponding temperature (or time). An example is shown in Figure 2.

The ratio of the areas for the data plotted in Figures 1 and 2 is about 32:1. On the assumption of equimolar sensitivities, this ratio represents the relative abundances of components corresponding to the two molecular masses and elemental compositions. The data do not distinguish between isomers unless differences in volatility are sufficient to produce distinguishable curves. Usually, this is not the case, especially when complex mixtures are being distilled.

Regression analysis on the data shown in Figure 2 either was terminated by matrix inversion errors (indicated on the terminal screen) or produced a goodness of fit (R^2) less than the minimum allowed value (0.8), which was entered from the terminal during execution of the program. When either situation occurs, the program plots the data points only and calculates non-statistical parameters to represent the data set. The T(IMAX) value is simply the temperature (or time) corresponding to the maximum intensity and the area is that obtained by adding the areas of trapezoids, as explained previously. The temperature (or time) centroid is calculated by adding the temperature-intensity (or time-intensity) products and dividing by the sum of the intensities. It is evident that T(IMAX) and T(CENTR) will converge when the distribution of data points becomes Gaussian; therefore, the difference between the two (29.03 K for the data shown in Figure 2) is an indication of data skewing and, usually, of the amount of data scatter when the results of the regression analysis are omitted.

SRCFR5. 11/26/86. SRC-II >325 DEG C STRONG ACIDS, FRACTION 5 SCANS: 50-120
 MAXIMUM PPM ERROR = 6.0 ELEMENTAL COMPOSITION: C(N)H(2N+2)O(2)
 Z = -26 MASS = 286. MINIMUM ALLOWED VALUE OF R**2 = 0.800
 IMAX/10000 = 2.44 T(IMAX) = 519.00 K T(CENTR) = 548.03 K AREA/10000 = 285.53

FIGURE 2. - Data plotted for the probe microdistillation of $C_{20}H_{14}O_2$, $M = 286$, from acids subfraction No. 5 isolated from the >325° C distillate of an SRC-II coal liquid. Ion current in arbitrary units vs. temperature in Kelvin.

Program "ELMCRV" produces a separate output file, "ELMCRV1.OUT", in which a table is printed showing the T(IMAX), IMAX, AREA, and other information for each ion arranged in order of decreasing z number and increasing mass. Ninety percent confidence intervals are included with the statistical output. Table I shows the results for molecular ions of elemental combination $C_nH_{2n+z}O_2$ originating from the acids subfraction of the SRC-II coal liquid. Including the results given in Table II, to be discussed below, compounds of this type were detected over a molecular-mass range from m/z 172 to m/z 442 and in corresponding z series from -14 to -40. The output has been edited to remove fragment ions and a few extraneous ions believed to arise either from the reference mixture used for mass assignment or from rearrangement mechanisms taking place in the molecular ions from the sample. Both this table and Table II below, are formatted for easy editing to remove any ions that do not belong in the homologous molecular-ion series.

Comparison of the areas under the curves provides an estimate of the relative abundances of the components of the given elemental combination. By far, the most abundant compound type is $C_{13}H_{12}O_2$, whose z number and molecular mass are -14 and 200 amu, respectively. This composition corresponds to isomers of methyl dihydroxybiphenyl. The confidence interval on the area represents a relative error of 7.4 %. Errors on the areas and other quantities increase dramatically as the abundances decrease toward zero, as seen for m/z 172, the first member detected in the $C_nH_{2n-14}O_2$ series. Because the first member of the dihydroxybiphenyl homologs has a molecular mass of 186, the compound(s) of mass 172 in the -14 z series must belong to some other type. If equimolar sensitivities can be assumed, the abundance of this type is only 0.10 % of the abundance of the methyl dihydroxybiphenyls.

The T(IMAX) of a molecular ion in a homologous series is inversely proportional to its relative volatility; thus, T(IMAX) increases with increasing carbon number (2). This is evident for intense molecular ions having narrow confidence intervals around their T(IMAX) values, as seen for m/z 186, 200, and 214 in the -14 z series. A increase of about two to six degrees is typical for sequential members of a series. This small, but significant, difference is oftentimes sufficient to determine whether an ion does not belong in a series; however, the converse is not true, i.e., an ion may have a T(IMAX) that appears to fit with the other values for a series, yet correspond to a different compound type.

TABLE I. - Edited output from program "ELMCRV" showing statistical results for $C_nH_{2n+2}O_2$ assignments from seventy scans of the high-resolution mass spectrum of an acids subfraction from an SRC-II coal liquid(a)

SRCFR5. 11/26/86. SRC-II >325° C STRONG ACIDS, FRACTION 5 SCANS: 50-120

MAXIMUM PPM ERROR = 6.0 ELEMENTAL COMPOSITION: $C_nH_{2n+2}O_2$

STATISTICAL RESULTS ORDERED BY DECREASING Z NUMBER AND INCREASING MASS

Z	M/Z	T(IMAX), K	IMAX/10000	AREA/10000	NO. PTS.
-14	172.	399.94 +- 41.20	0.68 +- 0.70	36.22 +- 58.60	5
-14	186.	404.90 +- 0.29	148.66 +- 8.78	9213.25 +- 581.34	39
-14	200.	406.95 +- 2.11	682.18 +- 34.92	35480.75 +- 2607.88	44
-14	214.	416.79 +- 1.10	107.14 +- 3.00	6915.78 +- 275.03	49
-14	228.	422.69 +- 0.50	13.52 +- 0.78	950.53 +- 57.95	40
-16	226.	419.54 +- 3.98	22.34 +- 5.66	2174.52 +- 599.34	58
-18	210.	461.77 +- 4.26	3.16 +- 1.46	554.13 +- 263.52	27
-18	224.	486.70 +- 14.20	5.25 +- 1.99	508.84 +- 202.73	31
-18	238.	467.45 +- 0.74	13.37 +- 0.94	1071.96 +- 78.32	29
-18	252.	465.68 +- 2.07	22.63 +- 5.43	1677.27 +- 414.43	37
-18	266.	466.31 +- 0.60	12.95 +- 0.83	1034.15 +- 68.54	23
-18	280.	467.19 +- 1.78	5.04 +- 0.79	302.05 +- 85.66	20
-20	250.	461.71 +- 0.19	9.19 +- 0.89	878.94 +- 154.17	25
-20	264.	476.55 +- 5.70	7.38 +- 1.77	671.66 +- 361.56	22
-20	278.	458.05 +- 9.17	8.40 +- 1.61	818.32 +- 270.76	14
-20	292.	475.99 +- 4.99	3.78 +- 1.02	402.84 +- 119.23	18
-20	306.	476.36 +- 2.55	1.52 +- 0.17	177.23 +- 41.98	15
-22	262.	469.95 +- 5.87	9.00 +- 0.88	846.16 +- 113.88	23
-22	276.	470.20 +- 0.55	18.94 +- 2.43	1540.98 +- 213.80	24
-22	290.	474.44 +- 0.51	12.03 +- 2.91	1039.00 +- 259.46	31
-22	304.	478.70 +- 16.40	5.43 +- 1.79	536.45 +- 186.52	26
-22	318.	478.74 +- 1.37	2.33 +- 0.31	161.70 +- 54.96	6
-24	274.	479.81 +- 3.79	2.99 +- 0.25	480.71 +- 60.45	28
-24	288.	480.90 +- 4.52	4.25 +- 1.25	820.17 +- 267.68	22
-24	302.	493.33 +- 14.55	5.77 +- 1.93	691.32 +- 242.35	25
-24	316.	482.73 +- 6.46	4.53 +- 1.25	581.80 +- 172.36	20
-26	300.	516.84 +- 8.12	3.62 +- 1.84	417.76 +- 222.01	21
-26	314.	533.33 +- 6.10	3.67 +- 1.27	344.02 +- 123.86	18
-26	328.	514.26 +- 6.21	3.21 +- 0.30	343.07 +- 79.59	14
-26	342.	500.56 +- 3.25	2.34 +- 0.79	256.83 +- 95.48	15
-28	312.	537.55 +- 9.58	6.16 +- 2.70	337.46 +- 439.72	11
-28	326.	517.12 +- 16.47	6.92 +- 1.52	727.85 +- 173.53	24
-28	340.	526.96 +- 12.46	5.00 +- 2.04	513.51 +- 214.13	23
-28	354.	544.16 +- 2.34	2.41 +- 0.27	289.60 +- 34.51	13
-30	324.	529.30 +- 2.23	2.09 +- 0.20	298.55 +- 41.76	13
-30	352.	537.31 +- 3.47	2.47 +- 0.98	334.93 +- 138.57	26
-30	366.	534.13 +- 2.81	2.47 +- 1.11	289.64 +- 135.10	21

(a) Results for fragment ions and several extraneous ions have been excluded.

TABLE II. - Edited output from program "ELMCRV" showing non-statistical results for $C_nH_{2n+Z}O_2$ assignments from seventy scans of the high-resolution mass spectrum of an acids subfraction from an SRC-II coal liquid^(a)

SRCFR5. 11/26/86. SRC-II >325° C STRONG ACIDS, FRACTION 5 SCANS: 50-120

MAXIMUM PPM ERROR = 6.0 ELEMENTAL COMPOSITION: $C_nH_{2n+Z}O_2$

NON-STATISTICAL RESULTS ORDERED BY DECREASING Z NUMBER AND INCREASING MASS

Z	M/Z	T(CENTR), K	T(IMAX), K	IMAX/10000	AREA/10000	NO. PTS.
-14	242.	530.74	432.00	3.00	400.08	25
-14	256.	514.54	416.00	0.88	117.81	16
-16	184.	524.70	393.00	0.97	194.16	16
-16	198.	548.57	456.00	8.47	1231.84	39
-16	212.	521.18	464.00	12.44	1824.61	39
-16	240.	548.63	432.00	8.74	1084.65	37
-16	254.	562.62	440.00	2.94	519.49	29
-16	268.	563.53	479.00	1.24	226.57	15
-16	282.	542.87	440.00	1.04	154.25	15
-18	196.	449.29	385.00	1.55	169.24	19
-18	294.	526.87	479.00	1.87	182.91	13
-20	236.	513.46	448.00	4.50	541.05	37
-20	320.	519.33	479.00	0.73	48.63	5
-22	234.	567.19	519.00	1.74	180.76	19
-22	248.	587.67	495.00	1.32	227.78	16
-22	332.	520.13	463.00	0.73	109.72	8
-24	246.	491.76	456.00	1.92	175.73	8
-24	260.	568.41	479.00	1.13	192.98	14
-24	330.	543.18	502.00	2.51	369.10	17
-24	344.	565.89	542.00	0.97	128.89	8
-26	272.	563.30	519.00	1.12	149.56	9
-26	286.	548.03	519.00	2.44	285.53	18
-26	356.	536.14	542.00	1.05	162.25	13
-26	370.	532.43	605.00	0.51	44.68	6
-28	284.	546.87	534.00	0.97	126.77	7
-28	298.	582.94	519.00	0.75	106.12	10
-28	368.	544.95	526.00	1.64	194.22	11
-28	382.	541.64	534.00	0.71	71.57	5
-30	310.	560.44	558.00	2.24	266.14	15
-30	338.	590.22	558.00	2.97	352.73	23
-30	380.	571.88	542.00	1.34	155.24	9
-30	394.	551.09	526.00	0.65	100.20	5

(a) Results for fragment ions and several extraneous ions have been excluded.

TABLE II. - Edited output from program "ELMCRV" showing non-statistical results for $C_nH_{2n+Z}O_2$ assignments from seventy scans of the high-resolution mass spectrum of an acids subfraction from an SRC-II coal liquid^(a) (contd)

SRCFR5. 11/26/86. SRC-II >325° C STRONG ACIDS, FRACTION 5 SCANS: 50-120

MAXIMUM PPM ERROR = 6.0 ELEMENTAL COMPOSITION: $C_nH_{2n+Z}O_2$

NON-STATISTICAL RESULTS ORDERED BY DECREASING Z NUMBER AND INCREASING MASS

Z	M/Z	T(CENTR), K	T(IMAX), K	IMAX/10000	AREA/10000	NO. PTS.
-32	336.	604.83	597.00	0.62	98.05	6
-32	350.	602.26	518.00	0.83	150.73	14
-32	364.	580.73	550.00	1.70	216.97	9
-32	378.	592.48	558.00	1.36	164.21	13
-32	392.	552.40	550.00	0.99	143.79	7
-32	406.	575.41	542.00	0.88	93.90	5
-34	348.	587.90	526.00	0.50	76.12	6
-34	362.	585.27	573.00	1.43	190.95	8
-34	376.	575.37	565.00	2.18	208.03	13
-34	390.	601.03	557.00	1.92	191.18	11
-34	404.	558.24	605.00	1.42	237.42	9
-36	360.	582.96	518.00	0.48	79.11	7
-36	388.	635.11	621.00	1.16	117.46	8
-36	402.	610.82	573.00	1.26	135.53	10
-36	416.	581.05	565.00	1.74	129.15	9
-36	430.	589.59	557.00	0.65	90.86	6
-38	386.	610.10	597.00	0.64	86.18	6
-38	400.	644.08	549.00	0.56	112.32	6
-38	414.	638.14	684.00	1.08	125.93	11
-38	428.	611.62	613.00	0.92	90.60	5
-38	442.	590.17	581.00	0.75	82.33	6
-40	412.	659.94	660.00	0.73	40.92	5
-40	426.	663.02	660.00	0.43	79.67	5
-40	440.	614.32	597.00	1.05	121.02	6

(a) Results for fragment ions and several extraneous ions have been excluded.

Non-statistical results, i.e., temperature (or time) centroids, etc., are printed in a separate table at the end of the "ELMCRV1.OUT" file. For the $C_nH_{2n+z}O_2$ assignments from the acids subfraction, the results are shown in Table II. By comparison with the results in Table I, those in Table II generally correspond to less abundant compounds. Consequently, scatter on the quantities given in the second table is greater. The results are significant, however, showing the presence of compound types having molecular masses from 184 to 442 in z series from -14 to -40. Results in the two tables can be combined to obtain the overall distribution of compound types detected. For example, m/z 242 and m/z 256 in the -14 z series in Table II belong with the more abundant members listed in Table I. Thus, seven members in the -14 z series of elemental combination $C_nH_{2n+z}O_2$ were detected. Similarly, eight members were detected in the -16 z series and seven in the -30 z series of the same combination.

Although the $C_nH_{2n+z}O_2$ compound types presented in Tables I and II comprise most of the acids subfraction No. 5 from the SRC-II coal liquid, other types of lesser quantities are known to be present from a detailed examination of the data. These minor components are not of interest to the present discussion and no further mention of their significance is given.

REFERENCES

1. Green, J. B.; Thomson, J. S.; Yu, S. K-T.; Treese, C. A.; Stierwalt, B. K.; Renaudo, C. P. ACS Div. Fuel Chemistry Preprint, 1986, Vol. 31, No. 1, 198-213.
2. Schronk, L. R.; Grigsby, R. D.; Scheppele, S. E., Anal. Chem., 1982, 54, 748-755.
3. Scheppele, S. E.; Grindstaff, Q. G.; Grigsby, R. D.; Chung, K. C.; Hwang, C. S.; Marriott, T. D.; Schronk, L. R. "Automated Probe Microdistillation/Mass Spectrometry for Analysis of High-Molecular Weight Compounds in Fossil Fuels," DOE/BETC/TPR-82/1, August, 1982, 22 pp.