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THE STRUCTURE OF COAL: NEW APPROACHES TO
CHARACTERIZING ORGANONITROGEN AND ORGANOSULFUR
FUNCTIONALITIES IN COAL AND COAL LIQUIDS
Final Report

By
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Work Performed Under Contract No. FG22-81PC40780

Purdue University
West Lafayette, Indiana

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FINAL REPORT

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CHARACTERIZING ORGANONITROGEN AND ORGANOSULFUR
FUNCTIONALITIES IN COAL AND COAL LIQUIDS

DE-FG22-81-PC40780

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ACKNOWLEDGMENT

The support of Conoco to the Purdue Research Laboratory is gratefully acknowledged.

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PROJECT TITLE: The Structure of Coal: New Approaches to Characterizing
Organonitrogen and Organosulfur Functionalities in Coal
and Coal Liquids. DE-FG22-81-PC40780

This report describes the application of tandem mass spectrometry (MS/MS) to the analysis of coal-related materials. A Finnigan Triple State Quadrupole mass spectrometer was used for most of the results obtained in this study. Both collision energy (0-30 eV) and collision gas pressure (0-2.5 mtorr, typically argon) have significant effects on the spectra. Increasing the collision energy or collision pressure results in an increased fragmentation of the selected ion. The analytical utility of different chemical ionization (CI) reagent gases is shown. The MS/MS spectra of a selected ion obtained by isobutane and ammonia CI are identical, which paves the way for development of MS/MS libraries. A library is being developed especially for the analysis of coal-related materials. Three principal MS/MS scan modes (daughter, parent and neutral loss) are utilized in the analysis of coal-related materials. Parent and neutral loss scans characterize the complex mixture for particular chemical moieties (functional groups, structure type), while daughter scans are used for identification of specific components. SRC II was the principal sample studied by CI. Laser desorption methodology for coal analysis was developed. Other fuel-related materials were examined to generalize the analytical methodology being developed for the coal-related materials, including shale oil and diesel exhaust particulates.

INTRODUCTION

The emphasis of the work reported is on characterizing heteroatom containing constituents of fuel-related materials utilizing new mass spectral methodologies. In particular, a newly purchased triple quadrupole mass spectrometer was utilized for the technique of mass spectrometry/mass spectrometry (MS/MS). In addition to providing information on targeted constituents alternate scanning techniques were utilized to investigate and further characterize the complex mixture of functional groups present in the coal-derived liquids. The work described below covers two main activities, analytical methods development in tandem mass spectrometry on the one hand and the application of these techniques in the fuels area.

Application of MS/MS to complex mixtures is no longer new⁽¹⁻⁵⁾ and it has come to be applied to a wide range of problems, from biochemical and pharmacological systems⁽⁶⁻⁹⁾ to environmental problems⁽¹⁰⁻¹¹⁾. This broad spectrum of applications results from the advantages inherent in MS/MS including rapid analysis, sensitivity, compound specificity, as well as low level quantitation capabilities. The speed of analysis follows from the nature of MS/MS, in which a complex mixture is transformed into a mixture of ions through a selected ionization process, typically chemical ionization. This mixture of ions is separated by mass-to-charge ratio and individual constituents can then be analyzed. This can be done in a number of different ways, most methods making use of the collisionally activated dissociation (CAD) which occurs in a collision cell located between the two mass analyzers.

A feature of the work reported here has been the attempt to further broaden the scope of MS/MS, improving characterization of samples by utilizing a range of operating conditions. The effect of collision energy on MS/MS spectra is the subject of particular interest because it provides additional information useful in compound identification. This work not only makes use of the triple quadrupole, which is a low energy collision system (variable 0-30 electron volts), but also a dual sector mass spectrometer which is capable of high energy (kilovolt range) collisions. Another area in which new ground was broken was in the combination of new ionization methods, specifically secondary ion mass spectrometry (SIMS) and laser desorption (LD), with tandem mass spectrometry. These methods make it possible to ionize thermally labile and involatile compounds and thereby greatly to extend the power of mass spectrometry. When applied to complex materials, MS/MS is a natural partner to the desorption ionization methods. The work on the combined methodology reported here therefore has broad value. In addition, it is particularly important as technological interest extends from the volatile coal-derived liquids to less volatile yet equally complex asphaltenes and related materials.

RESULTS AND DISCUSSION

The Finnigan Triple stage quadrupole mass spectrometer⁽¹²⁾ was the primary MS/MS system used for the results obtained in this work. The triple quadrupole consists of three co-axially arranged quadrupole rod assemblies. The first and third are conventional quadrupole mass analyzers. The middle quadrupole is operated in the rf only mode and is used as a focussing collision cell (Figure 1). The sample is volatilized

THE TRIPLE QUAD

FIGURE 1. Schematic diagram of the Finnigan Triple Quadrupole Mass Spectrometer.

and ionized in the ion source, usually with chemical ionization. An ion is mass selected with the first quadrupole, passes (with a controlled axial kinetic energy) into the collision cell (maintained at a given pressure) where it undergoes collisionally activated dissociation (CAD). The resulting fragment ions are then mass analyzed with the third quadrupole to obtain the MS/MS spectrum of the ion selected. Quadrupole MS/MS spectrometers are low energy collision systems as compared with sector type MS/MS spectrometers in which high energy collisions occur. Figure 2 shows the comparison of MS/MS spectra of the same precursor species. The high energy spectrum was obtained on a reverse geometry mass-analyzed ion kinetic energy (MIKE) spectrometer (magnetic analyzer followed by an electrostatic analyzer, Figure 3) operated at a collision energy of 7000 eV. The low collision energy spectrum taken with the quadrupole MS/MS spectrometer refers to a collision energy of 20 eV. These collision energies reflect the axial kinetic energy of the selected ion as it enters the collision cell. The differences between these two spectra are evident, the mass resolution in the low collision energy system enables adjacent peaks to be easily separated, whereas the high collision energy spectrum consists of broad unresolved peaks. The high collision energy system results in more complete fragmentation of the chosen molecule unlike the less energetic low collision energy process. The higher energies can be used on stable aromatic species to induce fragmentation whereas only the lower collision energies are needed to obtain significant fragmentation in alkyl or cycloalkyl systems. Of particular importance however, is the similarity between the two spectra in terms of the higher mass fragment ions. These spectra are typical of any comparison between high and low

COMPARISON OF LOW AND HIGH ENERGY MS/MS

FIGURE 2. Comparison of the low and high energy collision MS/MS spectra of protonated 2-methyl-5,6-benzoquinoline.

Mass-analyzed Ion Kinetic Energy Spectrometer

FIGURE 3. Schematic diagram of the Mass-Analyzed Ion Kinetic Energy (MIKE) Spectrometer.

collision energy spectra, the chief difference between which is the amount of energy transferred to the fragmenting ion rather than the types of reactions which occur^(13,14).

Collision Energy Effects

The quadrupole MS/MS system was found to have one unique characteristic that does distinguish it from a high collision energy system. This relates to the variability in MS/MS spectra as a function of the collision energy (Figure 4), and the collision pressure (Figure 5). As can be seen from the typical data shown this effect is quite dramatic⁽¹⁵⁻¹⁷⁾. Substantial and structurally diagnostic changes occur as the collision energy is varied from 8 eV to 20 eV for the MS/MS spectrum of protonated methyl quinoline. Similar effects are seen for collision pressure as it is varied from 0.5 mtorr Argon to 2.3 mtorr Argon for the MS/MS spectrum of protonated 2-methyl-5,6-benzoquinoline. This variability can be turned into an advantage in setting up an analytical scheme for the analysis of a particular component in a complex mixture as the dependence of MS/MS spectra as a function of energy and pressure can be utilized to enhance the specificity for a certain compound or class of compounds.

Reagent Gas Effects

Another aspect of low resolution quadrupole MS/MS is experiments aimed at achieving the desired degree of selectivity in the ionization step so as to minimize the number of possible interfering isobaric species occurring at the same nominal mass. We investigated several ways of doing this including specific chemical ionization (CI) reagent gases as well as using

FIGURE 4. MS/MS Spectra of protonated 4-methylquinoline as a function of collision energy from 8-20 eV. Argon collision pressure was 2.0 mtorr. FI/TI represents the ratio of fragment ion intensity to total ion intensity.

FIGURE 5. MS/MS spectra of protonated 2-methyl-5,6-benzoquinoline at two different argon collision pressures 0.5 mtorr and 2.3 mtorr. Collision energy was 20 eV.

both positive ion and negative ion detection. Figure 6 shows the chemical ionization mass spectrum of an SRC II fraction using ammonia and isobutane as the reagent gases. As would be expected ammonia CI is selective to nitrogen containing species and hence the observed increase in abundances of the even-molecular weight ions (due to nitrogen compounds) in the mass spectrum^(13,18,19). Figure 7 shows the MS/MS spectrum that is obtained for a particular nitrogen compound, protonated 6-aminochrysene, using both ammonia and isobutane as the CI reagent gas. The two reagent gases give the same protonated form of the molecule and therefore the same MS/MS spectra. This is an important result since it demonstrates that MS/MS spectra are insensitive to the method of ionization so that an authentic need not be run for each reagent gas in order to build a library of MS/MS spectra^(13,19). (Libraries are essential for interpretation of large volumes of data and library development was an important part of this work). Negative ion CI provides a further degree of selectivity in terms of the types of ions produced in the ion source⁽²⁰⁻²²⁾. However, characterization of negatively charged ions by MS/MS can sometimes be difficult. This results because negative ions can be easily neutralized in the collision cell and therefore often do not exhibit many intense ions in the MS/MS spectrum. The contrast between the negative and positive ion CIMS spectra of benzoic acid can be seen in Figure 8. The degree to which NICIMS can be used to selectively ionize certain compound classes compensates for the limited MS/MS information.

Alternative Scan Modes

FIGURE 6. Comparison of the isobutane and ammonia chemical ionization mass spectra of an SRC II sample.

CIMS/MS 6-AMINOCHRYSENE

FIGURE 7. Comparison of the isobutane and ammonia chemical ionization MS/MS spectra of protonated 6-aminochrysene. Collision energy was 20 eV and argon collision pressure was 2.0 mtorr.

FIGURE 8. Comparison of the positive ion (m/z 123) and the negative ion (m/z 121) chemical ionization MS/MS spectra of benzoic acid. Collision energy was 20 eV and argon collision pressure was 2.0 mtorr.

Up to this point in the report the emphasis has been on MS/MS spectra for selected ions produced in the ion source, these are called daughter spectra. While this is a valuable scanning mode for MS/MS, particularly for the identification of specific components in complex mixtures, other modes are available (Table 1) and can be even more useful^(10,20). In fact two other major scanning modes are of particular value because of their capabilities for characterizing the entire complex mixture for particular chemical moieties. These scanning modes are parent and neutral loss scans, (Figure 9). A parent scan is obtained by setting the second mass analyzer to pass a chosen fragment ion of interest and then scanning the first mass analyzer. In this manner only those ions which are passed by the first mass analyzer and subsequently fragment to the chosen ion are detected. This enables the complex mixture to be screened for a selected moiety. This capability is demonstrated in Figure 10 which is a parent scan of m/z 33 (HS^-) of an SRCII sample analyzed under negative ion chemical ionization conditions. This spectrum characterizes those components of the sample which have the SH moiety. As can be seen in Figure 10 there are three major ions m/z 109, 123 and 137. These masses correspond to the $\text{C}_0\text{-C}_2$ thiophenoxy [$\text{C}_6\text{H}_5\text{-S}^-$] ions. However, this test alone does not confirm the presence of $\text{C}_0\text{-C}_2$ thiophenols in the sample, but rather it indicates the presence of compounds which fragment to the thiophenoxy ion in the ion source prior to the first stage at mass analysis. Disulfides as well as thiophenes can be expected to give positive results in this test.

A second type of alternate scanning mode which is available, neutral loss scans, can be obtained by scanning the two mass analyzers

Table 1. MS/MS Experiments

Possible Experiments	Configuration		
	Q1	Q2	Q3
Daughter	SET	CAD	SCAN
Parent	SCAN	CAD	SET
Neutral Loss	SCAN	CAD	SCAN

where CAD stands for Collisionally Activated Dissociation.

TYPES OF MS/MS SPECTRA

DAUGHTER SPECTRUM

CHARACTERIZES A SELECTED
COMPOUND

PARENT SPECTRUM

CHARACTERIZES A SELECTED
MOIETY

NEUTRAL LOSS SPECTRUM

CHARACTERIZES A SELECTED
FUNCTIONAL GROUP

FIGURE 9. Schematic representation of the three principal MS/MS scanning modes.

FIGURE 10. Negative ion parent scan of HS^- , m/z 33^- from SRC II sample by isobutane chemical ionization, Collision energy was 20 eV and argon collision pressure was 2.0 mtorr.

simultaneously with a mass offset corresponding to the loss of a given neutral species in the CAD process. An example of a neutral loss scan is given in Figure 11. This spectrum characterizes the sample, an SRC II fraction, via the loss of H_2O in the CAD process which is a facile fragmentation pathway for protonated hydroxyaromatics. The sample was volatilized and ionized using positive ion isobutane chemical ionization while the two mass analyzers were scanned with an offset of 18 amu. Four major peaks were detected corresponding to C_0-C_3 phenols, m/z 95, 109, 123 and 137. This type of scan can be made very rapidly and it provides an excellent way of surveying for particular groups of constituents. Of course, several different tests can be used for the same functional group to avoid false positives.

Libraries of MS/MS Spectra

The instrumental parameters accessible to a triple quadrupole spectrometer enable a sample to be probed in a number of ways. This has been shown above in a cursory way through the dependence of the MS/MS spectrum on collision energy, collision pressure, scanning techniques and even ionization modes. One of the primary focusses of MS/MS is the identification of the constituents in complex mixtures, making use of one or many of these parameters. To make secure identifications there is the need to have the MS/MS spectra of authentic compounds for comparison and confirmation. This follows from the dependence of MS/MS spectra on conditions and the fact that MS/MS spectra cannot be accurately predicted from a knowledge of CI or EI mass spectra. In consequence, the available libraries of mass spectral data compilations are of little use. For this

FIGURE 11. Positive ion neutral loss scan of 18 from SRC II by isobutane chemical ionization at a probe temperature of less than 100°C . Collision was 20 eV and argon collision pressure was 2.0 mtorr.

reason we have begun to generate a library of MS/MS data on authentic compounds. We have fixed the variable parameters on the triple quadrupole to maximize fragmentation, thereby maximizing the information available to allow confirmation of unknown ions in a complex mixture. The entire library, consisting of over one hundred and fifty spectra, is included in the report as Appendix 1. This library is still being expanded and is routinely used in the analysis, identification and subsequent confirmation of constituents in coal-derived liquid samples. Figure 12 shows a typical library match of an unknown component m/z in 203 an SRC II sample. Because of this heavy emphasis of our research interests the bulk of the compounds found in the library are related to the species found or expected in coal-derived liquids.

Methodology Development

The types of research problems which can be addressed using MS/MS are too numerous to delineate. However, a brief description of some experiments which have been performed on the triple quadrupole will be presented prior to further details of results obtained on the fuel-related materials, such as coal-derived liquids. The experiments which follow have implications for the continued development of the analytical methodology. The proton affinities of particular classes of compounds are accessible by a MS/MS method^(15,23,24). For carboxylates for example, this information is available by observing the MS/MS spectrum of a set of proton-bound dimer species. This is illustrated in Figure 13, which is the MS/MS spectrum of the proton-bound dimer between propionate and acetate. The larger intensity anion, propionate, signifies the carboxylate with the lower

MID LIBRARY SEARCH DATA: 26K7GA0001 # 11 BASE M/E: 203
 05/25/83 23:37:00 + 0:11 CALI: CAL0429Q3 # 1 RIC: 55871.

CONDS.: +/CI-ISOC4/CAD-AR/DAUGHTERS OF 203 /-
 # 7 TO # 16 SUMMED

157 SPECTRA IN LIBRARYMS SEARCHED FOR MAXIMUM PURITY
 92 MATCHED AT LEAST 1 OF THE 16 LARGEST PEAKS IN THE UNKNOWN

RANK	IN NAME
1	97 FLUORANTHENE ISO-PCI (M+H) Q2=-20.0V 2.2MT ARGON
2	80 PYRENE ISO-PCI (M+H) Q2=-20.1V 2.2MT ARGON
3	99 2,4-DIPHENYLTHIOPHENE ISO-PCI (M+H) Q2=-20.0V 2.2MT ARGON
4	61 TRIFLUOROACETYL DERIV 1,2,3,4-TETRAHYDROISOQUINOLINE ISO-PCI (M+H)
5	58 TRIFLUOROACETYL DERIV 1,2,3,4-TETRAHYDROISOQUINOLINE ISO-PCI (M+H)

RANK	FORMULA	M. WT	B. PK	PURITY	FIT	RFIT
1	C16. H10	202	203	817	988	817
2	C16. H10	202	203	814	986	814
3	C16. H12. S	236	204	229	271	333
4	C11. H10. O. N. F3	229	202	174	484	309
5	C11. H10. O. N. F3	229	202	140	378	356

FIGURE 12. Printout from the library search routine for the MS/MS spectrum of m/z 203 from an SRC I sample showing very good agreement with both pyrene and fluoranthene.

FIGURE 13. Triple quadrupole MS/MS spectrum of the negatively charged proton-bound dimer ion of acetate and propionate using argon as the target gas. The relative abundances of propionate and acetate indicate that the former has the lower proton affinity of the two bases.

proton affinity of the given pair. These results duplicate the results obtained previously in a high energy collision spectrometer. Similar results can be obtained for the proton affinities of nitrogen bases (Figure 14). In this manner, the thermochemistry of proton-bound dimers, in particular, and dimers in general can be investigated.

With the capability for varying collision energy in a low energy MS/MS spectrometer it is possible to obtain breakdown curves experimentally^(16,25,26). These curves represent mass spectra as a function of internal energy. This can be seen in Figure 15 for the MS/MS spectrum of the molecular ion of 2-pentanone. This type of information enables a direct comparison with theoretical breakdown curves to be made. This experiment represents the most explicit means of characterizing structures by mass spectral fragmentation. As a simple example, consider Figure 15 which refers to 2-pentanone. Points of equal abundance of the ions m/z 58 and m/z 43 which occur at a collision energy of 25 eV and an argon collision pressure of 2.2 mtorr characterize the fragmenting ion. Theoretical calculations predict this particular cross point to occur with 4.5 eV of internal energy deposited into the molecular ion. Therefore approximately 20% of the collision energy in the low energy collision process at 2.2 mtorr Argon collision pressure is imparted into the molecular ion. Similar studies can be undertaken by keeping the collision energy constant and changing the collision pressure.

Another extremely powerful use of the triple quadrupole is the investigation of complex mixtures containing naturally occurring isotopic components^(27,28). The different scanning modes, daughter, neutral loss and parent can all be used to provide information in such a way that (i)

FIGURE 14: MS/MS spectrum of the diaminated proton (m/z 133) formed from n-propylamine and sec-butylamine.

FIGURE 15. MS/MS spectrum of the molecular ion of 2-pentanone as a function of collision energy. Argon collision pressure was 2.2 mtorr.

natural isotope ratios are employed as part of the tests to characterize a structure and (ii) the complexity of the mixture can be simplified. Figure 16 shows the electron impact mass spectrum of a nitrogen bases extract of a coal-derived liquid which has been doped with 150 ppm of a trichlorodibenzo-p-dioxin isomer. The molecular weight of this compound is m/z 286 but the complexity of the mixture is such that it cannot be recognized in this sample, in spite of its characteristic isotopic pattern. Figure 16B is the neutral loss 63 amu spectrum of this sample. 63 amu represents the characteristic loss of COCl from chlorinated dibenzo-p-dioxins. In contrast to the mass spectrum this is a very clean spectrum, indicative of the presence of a trichlorinated dibenzodioxin in this complex mixture. Figures 16C and 16D are the daughter spectra of m/z 288, the $(M+2)^+$ ion, from the nitrogen bases extract sample and from authentic 1,2,4-trichlorodibenzo-p-dioxin. The similarity of the two MS/MS spectra confirms the presence of the low level trichlorodibenzodioxin spike in the sample. The $(M+2)^+$ ion was chosen for comparison purposes rather than the M^+ because it contains one ^{37}Cl atom as well as the remaining ^{35}Cl atoms and enables a determination of the number of chlorine atoms present on a given molecule if the molecule is an unknown, by observing the intensity ratios of the $(M-35)^+$ and $(M-37)^+$ fragment ions in the daughter ion spectrum. This description is just a small portion of the information which can be gleaned from a sample containing compounds with polyisotopic elements by MS/MS.

Another important issue that can be addressed using MS/MS relates to the actual site of protonation or alkylation on a molecule. This issue has been under intense investigation for many years both experimentally and

a) MASS SPECTRUM

c) DAUGHTER SPECTRUM
OF 288⁺

b) NEUTRAL LOSS OF 63

d) DAUGHTER SPECTRUM
OF 288⁺

1,2,4-trichlorodibenzo-p-dioxin

FIGURE 16. (a) Electron impact mass spectrum, (b) neutral loss 63 amu spectrum, (c) daughter spectrum, m/z 288, from a nitrogen bases extract from a solvent refined coal mixture spiked with 150 ppm 1,2,4-trichlorodibenzo-p-dioxin, and (d) daughter spectrum of m/z 288 derived from authentic 1,2,4-trichlorodibenzo-p-dioxin.

theoretically. MS/MS enables a comparison to be made of the MS/MS spectrum of the alkylated or protonated species with the corresponding MS/MS spectra of authentic compounds which would be structurally equivalent⁽²⁹⁻³¹⁾. An example of this can be seen in Figure 17. Figure 17 (top) is the MS/MS spectrum of methylated aniline using CH_3F (the $\text{CH}_3\text{FCH}_3^+$ ion) as the methylating reagent gas. Figure 17 (center) is the MS/MS spectrum of protonated p-toluidine which represents the structural equivalent to ring methylation of aniline. Figure 17 (bottom) is the spectrum of protonated N-methylaniline which represents the structural equivalent to substituent methylation of aniline. Comparing these two MS/MS spectra with the spectrum of methylated aniline (using fragment ions which are distinctive for the two model compounds, like m/z 91 for p-toluidine) it is possible to approximate the relative amount of ring: substituent methylation. For the case of aniline this was found to be 1:4, ring: substituent. The MS/MS technique can be used to investigate alkylation of any species of interest. Carrying out a similar experiment to investigate site of protonation is more difficult because of the mobility of the proton. However, using deuterated compounds attempts to determine the relative ring-substituent protonation have also been carried out. The results of these studies are that phenol is protonated and alkylated on the ring in the CI source, while aniline is protonated on the ring but alkylated on the heteroatom.

Complex Fuel-Related Mixtures

While the MS/MS investigations that have just been described provide invaluable information, they constitute a minor component of this work. The main emphasis of MS/MS has to do with the characterization and

FIGURE 17. Fragment ion spectra recorded for collision-induced dissociation of methylated aniline (top) and for ions which model ring-methylation (center) and substituent-methylation (bottom). 7000 eV collisions, MIKE spectrometer, precursor ion m/z 108.

identification of components present in complex mixtures. This has indeed been the focus of this study using the triple quadrupole. Investigation of fuel-related complex mixtures particularly coal-derived liquids has been central to our work, however, natural products studies have also used the triple quadrupole MS/MS system. In several studies, including the characterization of nutmeg⁽³²⁾, the ability to perform parent scans enabled the identification of heretofore unknown compounds. This example can be seen in Figure 18 which is the parent scans of m/z 193 and m/z 203 from nutmeg. Both m/z 193 and m/z 203 represent structurally different fragments of the two common moieties of diphenyl propanoids in nutmeg. Both structures had been identified in previous studies but in this MS/MS study the presence of an ion at m/z 355 which fragments to both m/z 193 and m/z 203 indicates not one component but two, one having the base structure of each of the fragment ions chosen. The former structure had previously been identified but the latter structure is completely new. The value of MS/MS parent scanning in particular, is apparent in this example. Figure 19 shows the low collision energy MS/MS spectrum of a known component in nutmeg compared with the corresponding high collision energy MS/MS spectrum as yet another example of the relative similarities of the two types of MS/MS.

Coal-derived liquids have been of particular interest to our research efforts for two reasons^(13,20). First, the need to better understand the complex chemical nature of these mixtures is important to the developing coal-derived liquids industry in process design, both for economic, as well as for environmental reasons. Secondly, coal-derived liquids provide the type of very complex mixture desired which is ideal to test the

FIGURE 18. Comparison of parent spectra of all ions which generate the m/z 193⁺ and m/z 203⁺ daughter ions.

FIGURE 19. Comparison of the low energy collision MS/MS spectrum (upper) of 401^+ from nutmeg with the high energy collision MS/MS spectrum (lower).

characterization and identification capabilities of the triple quadrupole mass spectrometer system. The approach which has been used in this research program has three main focal points. These major areas of emphasis which all fall under the general heading of the characterization of coal-derived liquids for polynuclear aromatic hydrocarbons (PNAs) and the oxygen, nitrogen and sulfur containing PNAs are: (i) ionization modes, (ii) identifications using daughter scans and (iii) alternate scanning techniques. They are discussed in turn below.

The mode of ionization employed in obtaining MS/MS spectra had to be investigated in this study for two reasons. The first and most apparent reason is that changing the mode of ionization increases the selectivity and specificity of the molecules being ionized in the complex mixture. Changes in the reagent gas were made for this reason (Figure 20) which is a comparison of the positive ion chemical ionization mass spectrum of a middle distillate of a SRC II coal-derived liquid using ammonia and isobutane as reagent gases. Ammonia selectively ionizes nitrogen-containing species relative to isobutane and this can be seen in Figure 20 by the increased relative intensity of the even-mass ions which are indicative of nitrogen-containing species. Similar enhancement in specificity can be obtained for other compound types with the appropriate choice of reagent gas. For example, an N_2O /isobutane mixture produces the OH^- reagent ion for negative ion chemical ionization which is selective for acidic compounds. However, the change of reagent gas for this added selectivity was not the only reason these types of studies were carried out in this research program. Rather these changes were made to see whether a change in reagent gas in the ionization of a given compound

FIGURE 20. Comparison of the isobutane and ammonia chemical ionization mass spectra of an SRC II sample.

at the same nominal mass resulted in a different MS/MS spectrum. If a molecule was ionized in two different ways and produced two different MS/MS spectra this would present major problems in the development of a library which is a prime necessity in being able to identify the compounds present in a coal-derived liquid. Comparison of the MS/MS spectra of protonated 10-methyl-5,6-benzacridine using both ammonia and isobutane chemical ionization is presented in Figure 21. The two spectra are identical, which is reassuring as regards the development of MS/MS libraries. Problems that might still exist in the analysis of a coal-derived liquid as a result of changing reagent gases can be seen in Figures 22 and 23. Both figures compare ammonia and isobutane chemical ionization MS/MS spectra of two different ions in a coal-derived liquid sample. The spectra of Figure 22 are identical while those shown in Figure 23 are different. This is not directly related to the change in reagent gas but rather to the relative abundance of the ionized nitrogen containing constituent of interest to the corresponding hydrocarbon at one mass less. These latter ions have a ^{13}C isotope contribution at the nominal mass of the nitrogen containing compound. In Figure 22 the ^{13}C contribution of the hydrocarbon is negligible relative to the nitrogen containing species and it therefore does not contribute to the MS/MS spectrum. On the other hand, in Figure 23 the ^{13}C version of the hydrocarbon does contribute significantly to the isobutane CI/MS/MS spectrum but not to the ammonia CI/MS/MS in which case the hydrocarbon has not been as effectively ionized.

We turn now to the second of the three objectives, the identification of specific components of interest using MS/MS. In this case the mass of the ion of interest is selected from the coal-derived liquid and an MS/MS

CIMS/MS 10-METHYL-5,6-BENZACRIDINE

FIGURE 21. Comparison of the isobutane and ammonia chemical ionization MS/MS spectra of 10-methyl-5,6-benzacridine. Collision energy was 20 eV and argon collision pressure was 2.0 mtorr.

CIMS/MS SRC II

FIGURE 22. Comparison of the isobutane and ammonia chemical ionization MS/MS spectra of the ion at m/z 244 in an SRC II sample. The similarity of the two MS/MS spectra is indicative of the lack of a significant contribution of the ^{13}C isotope of the m/z 243 ion.

RELATIVE ABUNDANCE

FIGURE 23. Comparison of the isobutane and ammonia chemical ionization MS/MS spectra of the ion at m/z 194 in an SRC II sample. The large difference in the two MS/MS spectra is indicative of a significant contribution of the ^{13}C isotope of the m/z 193 ion to the isobutane spectrum.

spectrum is obtained. This spectrum is then compared with the MS/MS spectrum of an authentic. Two examples of this are given in Figure 24 and 25. Figure 24 is the comparison of the MS/MS spectrum of m/z 144 from an SRC II fraction with the MS/MS spectra of three methylquinoline isomers. Figure 25 compares the MS/MS spectrum of m/z 157 from an SRC II fraction with the MS/MS spectrum of dimethylnaphthalene. As can be seen, in both cases there is good agreement between the unknown and the selected authentic(s) chosen. While similar comparisons and confirmations can be shown for a large number of compounds identified in an SRC II fraction this is not the most advantageous use of MS/MS technology. The real power of MS/MS for the characterization of complex mixtures arises from the use of the alternate scanning techniques such as neutral loss and parent scans. Neutral loss scanning is particularly suited for the characterization of coal-derived liquids, because it exploits a chosen fragmentation and in so doing characterizes the coal-derived liquids for all components which can fragment in the selected manner. This is a particularly valuable way for analyzing for heteroatom containing species. Figure 26 is the neutral loss 18 amu spectrum obtained from the low temperature (less than 100°C) volatilization of an SRC II fraction. This spectrum is very simple consisting of just four peaks m/z 95, 109, 123 and 137 which correspond to the $\text{C}_0\text{-C}_3$ phenols. Confirmation of this assignment can be seen in Figure 27 which shows the daughter spectra of each of these ions. Each of these spectra are very similar to the MS/MS spectra of the corresponding authentic compounds. While this is a simple case it points out the utility of neutral loss scans of 18 amu (loss of

FIGURE 24. MS/MS spectra of the 144^+ ion from SRC II and three methylquinoline isomers. These spectra have been normalized by the scaling factor shown such that the second most intense ion equals the molecular ion 144^+ .

FIGURE 25. Comparison of the isobutane chemical ionization MS/MS spectra of the ion at m/z 157 in an SRC II sample and protonated dimethylnaphthalene.

NEUTRAL LOSS of 18 SRC II

FIGURE 26. Positive ion neutral loss scan of 18 from SRC II by isobutane chemical ionization at a probe temperature of less than 100°C. Collision energy was 20 eV and argon collision pressure was 2.0 mtorr.

FIGURE 27. Isobutane chemical ionization MS/MS spectra of the ions m/z 95, m/z 109, m/z 123 and m/z 137 in SRC II which correspond to the C_0 - C_3 phenols. Collision energy was 20 eV and argon collision pressure was 2.0 mtorr.

H₂O) in characterizing an SRC II fraction for hydroxy aromatic compounds. A much more complex spectrum is obtained at a higher volatilization temperature in order to obtain evidence of high mass hydroxyaromatic constituents, this spectrum can be seen in Figure 28. While the interpretation of this spectrum is under active investigation it can be seen that higher molecular weight species which lose 18 amu in the CAD process are detected; Figures 29 and 30 are the MS/MS spectra of two of these ions. Figure 29 has tentatively been identified as containing components of hydroxybiphenyl/acenaphthene and C₃ alkyl naphthalene. Figure 30 had tentatively been identified as containing components of hydroxy fluorene and dihydromethylfluorene. The next step in this analysis is to selectively ionize for the hydroxy containing constituents using negative ion chemical ionization. This should allow a positive confirmation of the hydroxy-containing constituents.

Neutral loss scanning has also proved invaluable in the identification of nitrogen containing constituents in an SRC II fraction. This is accomplished through a neutral loss of 17 amu, which corresponds to the loss of ammonia (NH₃). Amino PNAs are of particular interest because of their reported mutagenicity and they are directly amenable to this CAD test. However, aza PNA's also lose NH₃ in the CAD process, though to a lesser extent. This presents a problem; while the presence of a nitrogen containing species is confirmed, it is not clear whether it is an aza or amino compound. Figure 31 is the neutral loss 17 amu spectrum of a nitrogen bases extract⁽³³⁾ of an SRC II. The principal components are alkyipyridines/alkylanilines and alkylazafluorenes (carbazoles)/alkylamino fluorenes. A further experiment was carried out in order to determine the

FIGURE 28. Positive ion neutral loss scan of 18 from SRC II by isobutane chemical ionization at a probe temperature of 200°C. Collision energy was 20 eV and argon collision pressure was 2.0 mtorr.

FIGURE 29. Isobutane chemical ionization MS/MS spectrum of the ion at m/z 171⁺ in a SRC II sample. Collision energy was 20 eV and argon collision pressure was 2.0 mtorr.

FIGURE 30. Isobutane chemical ionization MS/MS spectrum of the ion at $m/z\ 183^+$ in an SRC II sample. Collision energy was 20 eV and argon collision pressure was 2.0 mtorr.

FIGURE 31. Neutral loss scan of 17 from a non-derivatized nitrogen bases extract of an SRC II. Collision energy was 20 eV and argon collision pressure was 2.0 mtorr.

presence of amino constituents and hydro aza PNAs. This was done through trifluoroacetylation of the nitrogen bases extract such that only those nitrogen-containing species carrying replaceable hydrogens would be derivatized. Figure 32 is the comparison of the isobutane chemical ionization mass spectrum of the derivatized and nonderivatized nitrogen bases extract. Those compounds having undergone further selectivity through derivatization are either amino or hydro aza PNAs. Figure 33 confirms 1,2,3,4-tetrahydroquinoline in the derivatized nitrogen bases extract as well as the underivatized sample with the corresponding authentic.

The identification of organosulfur species in coal-derived liquids has also been investigated. Parent scans for m/z 33 (HS^-) in the negative ion mode (Figure 34) have been used to identify sulfide containing PNAs in an SRC II fraction. These conclusions have been confirmed by high collision energy MS/MS experiments using charge inversion (Figure 35). Charge inversion consists of negative ion ionization and mass selection followed by positive ion mass separation and detection of the fragment ions produced in the CAD process (Table 1). Further identification of aromatic sulfur has centered around the use of neutral loss scans. This has taken a number of avenues, neutral loss 33 amu (HS) and 44 amu (CS) (Figure 36), as well as correlation with the corresponding isotopic sulfur peak ^{34}S . Figure 36 is the MS/MS spectrum of protonated dibenzothiophene which shows both the HS loss (m/z 152) and the CS loss (m/z 141). Results have been only moderately successful and then only if the component of interest was present at a reasonable concentration. Confirmation of the suspected sulfur containing constituent with daughter ion spectra has been difficult.

FIGURE 32. Comparison of the isobutane chemical ionization mass spectra of a nitrogen bases extract from an SRC II before and after trifluoroacetyl derivatization.

IDENTIFICATION OF TETRAHYDROQUINOLINE

FIGURE 33. Identification of tetrahydroquinoline in a nitrogen bases extract of a SRC II by comparison of the MS/MS spectra of authentic tetrahydroquinoline with the corresponding ion in the nitrogen bases extract before (ion at m/z 134) and after (ion at m/z 230) trifluoroacetyl derivatization.

FIGURE 34. Negative ion parent scan of HS^- , (m/z 33) from SRC II sample by isobutane chemical ionization. Collision energy was 20 eV and argon collision pressure was 2.0 mtorr.

CHARGE INVERSION MS/MS

FIGURE 35. Chemical ionization charge inversion ($- \rightarrow +$) MS/MS spectra of m/z 109⁻ from SRC II and m/z 109⁻ fragment from thioanisole. Spectra taken at 7 kV accelerating potential on the MIKE spectrometer at a nominal probe temperature of 150°C. A mixture of nitrous oxide and isobutane was used as the chemical ionization reagent gas. The peaks at m/z 45⁺ and m/z 69⁺ suggest the presence of thioaryl moieties in the SRC II sample.

MS/MS Spectrum of 185^+ (MH^+ of Dibenzothiophene)

FIGURE 36. Isobutane chemical ionization MS/MS spectrum of protonated dibenzothiophene depicting the fragment ions resulting from loss of CS (m/z 141) and HS (m/z 152). Collision energy was 20 eV and argon collision pressure was 2.0 mtorr.

The neutral loss fragmentation is of such low intensity relative to other fragment ions that the presence of the sulfur containing species cannot be confirmed because of the great excess of other species at this given nominal mass. At this time other ways of selectively analyzing for sulfur containing species are being investigated in which the mass spectrometer is still the avenue for obtaining this selectivity. Alternatively rapid chemical pre separation schemes could be used to mitigate this problem.

Neutral loss and parent scanning are not only useful for characterization of heteroatom constituents in a complex mixture. Any neutral fragment that is lost can be scanned in order to characterize the complex mixture for the moiety that is lost in the collision process. Figure 37 is the neutral loss 15 amu spectrum of an SRC II fraction. This scan characterizes the sample for those components which have a methyl group. The major ions observed in this spectra correlate with C_1-C_x phenols and C_1-C_x naphthalenes. This example shows that neutral loss scanning is not limited to the loss of stable neutral fragments. Parent scanning can also be extremely useful in characterizing complex mixtures for specific compound classes even if they do not have a heteroatom functionality. An example of this can be seen in Figure 38 which is the parent scan of m/z 128. In this case all components which fragment to m/z 128, essentially the naphthalene ion, are detected. Therefore, this parent scan characterizes the SRC II fraction for those compounds having a structurally similar backbone viz. all naphthalenes. Other fragment ions can be chosen as well to characterize a complex mixture for the presence of a chosen structural moiety. To reemphasize, both neutral loss and parent scanning techniques are invaluable for a rapid characterization of selected

FIGURE 37. Neutral loss scan of 15 from a SRC II sample. Collision energy was 20 eV and argon collision pressure was 2.0 mtorr.

FIGURE 38. Parent scan for those ions which fragment to give an ion at m/z 128 in a SRC II sample. Collision energy was 20 eV and argon collision pressure was 2.0 mtorr.

structural moieties. Coupling this information with daughter ion spectra allows confirmation of the identity of the species of interest.

In addition to our studies of coal liquids, other fuel-related materials have been investigated using MS/MS including shale oils and diesel particulates. The shale oil samples⁽³⁴⁾ were investigated for a comparison with the coal-derived liquids, while the diesel particulates were studied in order to establish the viability of direct MS/MS analysis of the particulates, for the adsorbed organic constituents. The shale oil samples were obtained from modified Fischer assay retorting conditions (Table 2). Figure 39 is the isobutane CIMS of these materials. As would be expected the primary difference between the shale oil and coal-derived liquid material relates to the more aliphatic nature of the shale oils. A second major difference, at least between the sample types run in this study, is in the degree to which hydroxyaromatic compounds are absent. Both of these differences are apparent in Figure 40 which is the m/z 95 daughter spectrum from both the shale oil samples and the coal-derived liquids. As has been shown previously for the SRC II sample the primary constituent at this mass is protonated phenol. However, in the shale oil sample there is no evidence for phenol but instead fragmentations typical of aliphatic ions are observed. A second study was carried out to discover any differences in the nitrogen containing species present in the oil shale, particularly as the modified Fischer Assay retorting conditions were changed. Figure 41 shows the neutral loss 17 amu spectra for the two samples having the largest difference in heating rate. As can be seen, sample 413 (slowest heating rate) has essentially the same spectrum as sample 423 (fastest heating rate) except there is one extra very dominant

Table 2. Fischer Assay Retorting Conditions

<u>SAMPLE NO.</u>	<u>CONDITIONS</u>	<u>OIL YIELD, GAL./TON</u>
413	55°C/MIN	19.2
410	12°C/MIN	17.7
423	4°C/MIN	15.4
479	4°C/MIN + 0.7 L/MIN STEAM	17.2

FIGURE 39. Isobutane chemical ionization mass spectrum of a modified Fischer Assay retorted oil shale sample.

FIGURE 40. Comparison of the m/z 95 daughter spectra from a SRC II sample and an oil shale sample. The SRC II spectrum is consistent with phenol while the oil shale spectrum shows considerable aliphatic character. Collision energy was 20 eV and argon collision pressure was 2.0 mtorr.

FIGURE 41. Comparison of the neutral loss scan of 17 for a shale oil sample at two different conditions (in this case heating rates) of a modified Fischer Assay retort. Notice the additional series present beginning at m/z 128 in sample 423.

series of ions. Apparently this series of compounds is destroyed at the fastest heating rates. Figure 42 is the daughter spectrum, of the first member of this series, m/z 128 from both sample 413 and sample 423. As can be seen there is a strong loss of 17, possibly NH_3 , in sample 413 but no corresponding loss in the other sample as expected. The identification of this component has not yet been confirmed but the ability to obtain this type of differentiation points out the valuable nature of MS/MS in characterizing a set of complex samples as a function of some experimental or sample processing parameter.

The direct analysis of diesel particulates^(20,35) are also of interest both as a result of the environmental concern as the number of diesel transportation vehicles increases and to extend the MS/MS methodology to a solid sample matrix. Figure 43 shows the positive ion and negative ion isobutane chemical ionization mass spectrum of a diesel particulate. Figures 44-46 show the identification of specific components with authentic from a diesel particulate sample. Figure 44 is the daughter spectrum of m/z 143 which is confirmed as being predominately composed of methylnaphthalene isomers. Figure 45 is the daughter spectrum of m/z 193 which matches the spectrum of methylphenanthrene/anthracene isomers. Notice there is strong evidence for the presence of at least one other component as evidenced by the low mass fragment ions which are not present in the MS/MS spectrum of methylphenanthrene. Figure 46 is the MS/MS spectrum of m/z 257 which corresponds to palmitic acid as confirmed by the authentic spectrum. Figure 47 is a set of four MS/MS spectra making use of both positive ion and negative ion chemical ionization to confirm the identification of an unknown component in a diesel particulate sample.

FIGURE 42. Comparison of the isobutane chemical ionization MS/MS spectra for the ion at m/z 128 from a shale oil sample at two different conditions (heating rates) of a modified Fischer Assay retort. Collision energy was 20 eV and argon collision pressure was 2.0 mtorr.

CIMS DIESEL PARTICULATES

FIGURE 43. Positive and negative ion isobutane chemical ionization mass spectra of diesel particulate. Spectra were obtained by summing ca. 100 individual mass spectra acquired while the solid probe was heated from 50 to 400°C.

FIGURE 44. Comparison of the isobutane chemical ionization MS/MS spectrum of the ion at m/z 143 from a diesel particulate with the MS/MS spectrum of protonated 2-methylnaphthalene. Collision energy was 20 eV and argon collision pressure was 2.0 mtorr.

FIGURE 45. Comparison of the isobutane chemical ionization MS/MS spectrum of the ion at m/z 193 from a diesel particulate with the MS/MS spectrum of protonated methylphenanthrene. Collision energy was 20 eV and argon collision pressure was 2.0 mtorr.

FIGURE 46. Positive ion isobutane chemical ionization MS/MS spectra derived from diesel particulate and authentic palmitic acid. Collision energy was 20 eV and argon collision pressure was 2.0 mtorr.

FIGURE 47. a) Positive ion isobutane chemical ionization MS/MS spectra of m/z 139 derived from a diesel particulate and authentic p-hydroxybenzoic acid. b) Negative ion isobutane chemical ionization MS/MS spectra of m/z 137 derived from a diesel particulate and authentic p-hydroxybenzoic acid. Collision energy was 20 eV and argon collision pressure was 2.0 mtorr.

Figure 47A shows positive ion CIMS/MS spectra of m/z 139 from the diesel particulate and a possible authentic protonated hydroxybenzoic acid. Many of the ions in the unknown match but there are still many which do not indicating that presence of at least a second component besides hydroxybenzoic acid. For added confirmation of the hydroxybenzoic acid the negative ion CIMS/MS spectra, which gives added specificity, were obtained (Figure 47B). The added specificity arises because of the presence of acidic protons in hydroxybenzoic acid in which ionization occurs with the $(M-H)^-$ ion, m/z 137. This separates out the other components which either do not ionize, do not ionize at $(M-H)^-$ or do not fragment. The resulting negative ion CIMS/MS spectra (unknown and authentic) match, with the loss of CO_2 being the only fragment ion. This figure shows how the positive ion and negative ion CIMS/MS spectra can be used to enhance the reliability of the identification of an unknown in a complex mixture, such as a diesel particulate sample. Figure 48 is the neutral loss 18 amu (loss of H_2O in the collision process) spectrum obtained from a diesel particulate sample. Table 3 lists the tentative identification of some of the hydroxyaromatics indicated as being present from the neutral loss spectrum.

Finally, there is one important fuel-related material which has not been discussed. This is coal itself. A number of preliminary studies have been undertaken as a prelude to the direct structural analysis of coal, besides the work on coal-derived materials. These preliminary studies have dealt first, with completion of a laser desorption (LD) ionization assembly and second, with operation and optimization for coal volatilization. Use of the LD system on selected model compounds has been carried out. Figure

FIGURE 48. Neutral loss scan of 18 from a diesel particulate obtained with a fuel/air equivalence ratio of 0.5 at 1500 rpm for characterization of the hydroxy-containing constituents.

Table 3. Tentative Identification of Some Hydroxy
Containing Constituents in Diesel Exhaust
Particulate

$C_1 - C_3$ alkyl phenols	m/z 108, 122, 136
$C_0 - C_2$ alkyl indenols	m/z 132, 146, 160
$C_0 - C_1$ alkyl indanols	m/z 134, 148
$C_0 - C_1$ alkyl naphthanols	m/z 144, 158
$C_0 - C_1$ alkyl acenaphthenols/biphenols	m/z 170, 184
fluoreinol	m/z 182
phenanthranol/anthracenol	m/z 194

49 shows an initial mass spectrum obtained using these conditions from a Kentucky coal. Model compounds have been studied using LD/MS/MS and one such example is the LD/MS/MS spectrum of amino chrysene (Figure 50). The controlled chemical degradation and LD/MS/MS of coal is the subject of current DOE-supported research, which is predicated in large measure on the success achieved in the work covered in this report.

FIGURE 49. Laser desorption mass spectrum of Kentucky coal.

FIGURE 50. Laser desorption (pulsed Nd-yag laser) isobutane chemical ionization MS/MS spectrum of 6-aminochrysenes. Spectra taken at 7 kV accelerating potential on the MIKE spectrometer.

REFERENCES

1. Cooks, R.G.; Glish, G.L., Chem. Eng. News, 1981, Nov. 30, 40.
2. Kondrat, R.W.; Cooks, R.G., Anal. Chem., 1978, 50, 81A.
3. Maugh, T.H., Science, 1980, 209, 675.
4. McLafferty, F.W. Science, 1981, 214, 280.
5. Yost, R.A.; Enke, C.G., Anal. Chem., 1979, 51, 1251A.
6. Brotherton, H.O.; Yost, R.A., Anal. Chem., 1983, 55, 549.
7. Ciupek, J.D.; Cooks, R.G.; Chang, C.J., FDA Eighth Science Symposium on Recent Advances in Analytical Methodolgy in the Life Sciences, in press.
8. Perchalski, R.J.; Yost, R.A.; Wilder, B.J., Anal. Chem., 1982, 54, 1466.
9. Hunt, D.F.; Bone, W.M.; Shabanowitz, J.; Rhodes, J.; Ballard, J.M., Anal. Chem., 1981, 53, 1705.
10. Hunt, D.F.; Shabanowitz, J.; Anal. Chem., 1982, 54, 574.
11. Schuetzle, D.; Riley, T.L.; Prater, T.J.; Hunt, D.F.; Harvey, T.M., Anal. Chem., 1982, 54, 265.
12. Slayback, J.R.B.; Story, M.S.; Ind. Res./Dev., 1981, (Feb.), 129.
13. Ciupek, J.D.; Zakett, D.; Cooks, R.G.; Wood, K.V., Anal. Chem., 1982, 54, 2215.
14. Harvan, D.J.; Nystrom, J.A.; Grady, W.L.; Voyksner, R.D.; Czerny, R.L.; Bursey, M.M.; Siegel, M.W.; Yinon, J.; Hass, J.R.; Anal. Letters, 1981, 14, 985.
15. Wright, L.G.; McLuckey, S.A.; Cooks, R.G.; Wood, K.V., Int. J. Mass Spectrom. Ion Phys., 1982, 42, 115.

16. McLuckey, S.A.; Glush, G.L.; Cooks, R.G., Int. J. Mass Spectrom. Ion Phys., 1981, 39, 219.
17. Yost, R.A.; Euke, C.G.; McGilvery, D.C.; Smith, D.; Morrison, J.D., Int. J. Mass Spectrom. Ion Phys., 1979, 30, 127.
18. Buchanan, M.V., Anal. Chem., 1982, 54, 570.
19. Richter, W.J.; Schwarz, H., Angew. Chem., Int. Ed. Engl., 1978, 17, 424.
20. Ciupek, J.D.; Cooks, R.G.; Wood, K.V.; Ferguson, C.R., Fuel, in press.
21. Dougherty, R.C., Anal. Chem., 1981, 53, 625A.
22. Hunt, D.F.; Shabanowitz, J.; Giordani, A.B., Anal. Chem., 1980, 52, 386.
23. McLuckey, S.A.; Cameron, D.; Cooks, R.G., J. Am. Chem. Soc., 1980, 103, 1313.
24. Cooks, R.G.; in M.L. Gross (Ed.) High Performance Mass Spectrometry: Chemical Applications, ACS Symposium Series 70, Am. Chem. Society, Wash., D.C., 1978, Chap. 4.
25. McLuckey, S.A., Ph.D. Thesis, Purdue University, 1982.
26. Fetterolf, D.D.; Yost, R.A., Int. J. Mass Spectrom. Ion Phys., 1982, 44, 37.
27. Singleton, K.E.; Cooks, R.G.; Wood, K.V., Anal. Chem., 1983, 55, 762.
28. Todd, P.J.; Barbalas, M.P.; McLafferty, F.W., Org. Mass Spectrom., 1982, 17, 79.
29. Wood, K.V.; Burinsky, D.J.; Cameron, D.; Cooks, R.G., submitted.

30. Miller, D.L.; Lay, Jr., J.O.; Gross, M.L.; J. Chem. Soc., Chem. Comm., 1982, 970.
31. Cacace, F., J. Chem. Soc. Perkin Trans., II, 1982, 1129.
32. Davis, D.V., Cooks, R.G., J. Agric. Food Chem., 1982, 30, 495.
33. Manuscript in preparation with Dr. Chuck Schmidt of PETC.
34. Wood, K.V., Presented at Eastern Oil Shale Symposium, Lexington, KY, October 1982.
35. Wood, K.V.; Ciupek, J.D.; Cooks, R.G.; Ferguson, C.R., SAE paper 821217.

APPENDIX I

LIST OF COMPOUNDS IN MS/MS LIBRARY

LIBRARYUS

INDEX:	NAME M.WT FORMULA (MASSES, INTENSITIES)	RET. TIME	R. R. T.	MASS	AMOUNT
1:	STEARIC ACID ISO-PCI (M+H) Q2=-20.4V 2.0MT ARGON 284 C18.H36.O2 (43, 783)(55, 299)(57, 1000)	0:00	0.000	0.	0.00
2:	2-PENTANONE PEI (M+) Q2=-20.0V 2.2MT ARGON 86 C5.H10.O (41, 90)(43, 946)(45, 49)	0:00	0.000	0.	0.00
3:	2-PENTANONE SLF-PCI (M+H) Q2=-20.0V 2.2MT ARGON 86 C5.H10.O (41, 63)(43, 30)(45, 1000)	0:00	0.000	0.	0.00
4:	THIOPHENOL ISO-PCI (M+H) Q2=-20.0V 2.0MT ARGON 110 C6.H6.S (51, 34)(55, 6)(57, 13)	0:00	0.000	0.	0.00
5:	THIOPHENOL ISO-NCI (M-H) Q2=22.9V 2.0MT ARGON 110 C6.H6.S (33, 34)(107, 2)(108, 1)	0:00	0.000	0.	0.00
6:	BENZOIC ACID ISO-PCI (M+H) Q2=-20.4V 2.0MT ARGON 122 C7.H6.O2 (45, 64)(55, 21)(67, 82)	0:00	0.000	0.	0.00
7:	NAPHTHALENE ISO-PCI (M+H) Q2=-20.3V 2.2MT ARGON 128 C10.H8 (51, 10)(77, 30)(78, 10)	0:00	0.000	0.	0.00
8:	2-THIOPHENECARBOXYLIC ACID ISO-PCI (M+H) Q2=-25V 1.6MT ARGON 128 C5.H4.O2.S (39, 56)(41, 147)(45, 439)	0:00	0.000	0.	0.00
9:	THIANAPHTHENE ISO-PCI (M+H) Q2=-20.0V 2.2MT ARGON 134 C8.H6.S (41, 1)(65, 9)(90, 6)	0:00	0.000	0.	0.00
10:	4-HYDROXYBENZOIC ACID ISO-PCI (M+H) Q2=-20.3V 2.2MT ARGON 138 C7.H6.O3 (41, 20)(45, 30)(51, 20)	0:00	0.000	0.	0.00
11:	P-HYDROXYBENZOIC ACID ISO-NCI (M-H) Q2=13.6V 1.7MT ARGON 138 C7.H6.O3 (93, 961)(137, 1000)	0:00	0.000	0.	0.00
12:	N-DECANE ISO-PCI (M+H) Q2=-20.4V 2.0MT ARGON 142 C10.H22 (41, 62)(43, 77)(55, 568)	0:00	0.000	0.	0.00
13:	2-METHYLNAPHTHALENE ISO-PCI (M+H) Q2=-20.3V 2.2MT ARGON 142 C11.H10 (77, 8)(78, 2)(91, 10)	0:00	0.000	0.	0.00
14:	2-METHYLQUINOLINE ISO-PCI (M+H) Q2=-20.3V 2.1MT ARGON 143 C10.H9.N (77, 442)(102, 46)(103, 712)	0:00	0.000	0.	0.00
15:	4-METHYLQUINOLINE ISO-PCI (M+H) Q2=-20.2V 2.2MT ARGON 143 C10.H9.N (77, 51)(91, 103)(103, 42)	0:00	0.000	0.	0.00

16:	7-METHYLQUINOLINE ISO-PCI (M+H) Q2=-20.3V 2.1MT ARGON 143 C10.H7.N (91, 79)(101, 7)(116, 18)	0:00 0.000 0.	0.00
17:	1-AMINONAPHTHALENE ISO-PCI (M+H) Q2=-20.3V 2.0MT ARGON 143 C10.H7.N (77, 10)(91, 32)(115, 56)	0:00 0.000 0.	0.00
18:	7-METHYLQUINOLINE NH3-PCI (M+H) Q2=-20.2V 2.3MT ARGON 143 C10.H7.N (91, 91)(101, 9)(115, 114)	0:00 0.000 0.	0.00
19:	1-AMINONAPHTHALENE NH3-PCI (M+H) Q12=-20.2V 2.4MT ARGON 143 C10.H7.N (77, 39)(91, 60)(115, 109)	0:00 0.000 0.	0.00
20:	1-PHENYLPYRROLE ISO-PCI (M+H) Q2=-20.3V 2.2MT ARGON 143 C10.H7.N (41, 257)(77, 691)(91, 305)	0:00 0.000 0.	0.00
21:	ANTHRACENE ISO-PCI (M+H) Q2=-20.3V 2.2MT ARGON 178 C14.H10 (128, 1)(151, 3)(152, 10)	0:00 0.000 0.	0.00
22:	5-METHYLCARBAZOLE ISO-PCI (M+H) Q2=-20.3V 2.1MT ARGON 181 C13.H11.N (39, 2)(139, 3)(140, 2)	0:00 0.000 0.	0.00
23:	5-METHYLCARBAZOLE NH3-PCI (M+H) Q2=-20.2V 2.3MT ARGON 181 C13.H11.N (53, 1)(139, 3)(140, 3)	0:00 0.000 0.	0.00
24:	2-AMINOFUORENE ISO-PCI (M+H) Q2=-20.3V 2MT ARGON 181 C13.H11.N (115, 20)(141, 20)(153, 9)	0:00 0.000 0.	0.00
25:	2-AMINOFUORENE NH3-PCI (M+H) Q2=-20.2V 2.4MT ARGON 181 C13.H11.N (115, 30)(141, 20)(153, 9)	0:00 0.000 0.	0.00
26:	DIBENZOTHIOPHENE ISO-PCI (M+H) Q2=-20.0V 2.2MT ARGON 184 C12.H8.S (115, 1)(139, 2)(141, 6)	0:00 0.000 0.	0.00
27:	1-METHYLPHENANTHRENE ISO-PCI (M+H) Q2=-20.3V 2.2MT ARGON 192 C15.H12 (55, 3)(128, 3)(151, 8)	0:00 0.000 0.	0.00
28:	9-METHYLANTHRACENE ISO-PCI (M+H) Q2=-20.2V 2.2MT ARGON 192 C15.H12 (115, 3)(151, 3)(152, 20)	0:00 0.000 0.	0.00
29:	2-METHYL-5,6-BENZOQUINOLINE ISO-PCI (M+H) Q2=-20.3V 2.1MT ARGON 193 C14.H11.N (151, 35)(152, 80)(153, 11)	0:00 0.000 0.	0.00
30:	2-METHYL-5,6-BENZOQUINOLINE NH3-PCI (M+H) Q2=-20.2V 2.3MT ARGON 193 C14.H11.N (151, 71)(152, 185)(153, 23)	0:00 0.000 0.	0.00
31:	2-PHENYLINDOLE ISO-PCI (M+H) Q2=-20.3V 2.1MT ARGON 193 C14.H11.N (91, 118)(116, 169)(117, 125)	0:00 0.000 0.	0.00
32:	1-AMINOANTHRACENE ISO-PCI (M+H) Q2=-20.3V 2MT ARGON 193 C14.H11.N (128, 22)(151, 23)(152, 31)	0:00 0.000 0.	0.00
33:	1-AMINOANTHRACENE NH3-PCI (M+H) Q2=-20.2V 2.4MT ARGON 193 C14.H11.N (128, 49)(151, 40)(152, 59)	0:00 0.000 0.	0.00

34:	9-AMINOPHENANTHRENE ISO-PCI (M+H) G2=-20.3V 2.2MT ARGON 193 C14.H11.N (116, 20)(151, 101)(152, 101)	0:00 0.000 0.	0.00
35:	THIANTHRENE ISO-PCI (M+H) G2=-25V 2.1MT ARGON 216 C12.H8.S2 (108, 54)(139, 8)(152, 20)	0:00 0.000 0.	0.00
36:	3-AMINOFUORANTHENE ISO-PCI (M+H) G2=-20.3V 2MT ARGON 217 C16.H11.N (165, 3)(178, 2)(189, 8)	0:00 0.000 0.	0.00
37:	3-AMINOFUORANTHENE NH3-PCI (M+H) G2=-20.2V 2.4MT ARGON 217 C16.H11.N (165, 14)(178, 4)(189, 22)	0:00 0.000 0.	0.00
38:	MYRISTIC ACID ISO-PCI (M+H) G2=-20.4V 2.0MT ARGON 228 C14.H28.O2 (41, 131)(43, 1000)(55, 191)	0:00 0.000 0.	0.00
39:	10-METHYL-5,6-BENZACRIDINE ISO-PCI (M+H) G2=-20.3V 2.1MT ARGON 243 C18.H13.N (202, 10)(216, 6)(217, 28)	0:00 0.000 0.	0.00
40:	10-METHYL-5,6-BENZACRIDINE ISO-PCI (M+H) G2=-20.2V 2.3MT ARGON 243 C18.H13.N (69, 9)(166, 10)(202, 11)	0:00 0.000 0.	0.00
41:	6-AMINOCHRYSENE ISO-PCI (M+H) G2=-20.3V 2MT ARGON 243 C18.H13.N (116, 12)(166, 8)(202, 48)	0:00 0.000 0.	0.00
42:	6-AMINOCHRYSENE NH3-PCI (M+H) G2=-20.2V 2.4MT ARGON 243 C18.H13.N (116, 57)(166, 34)(202, 189)	0:00 0.000 0.	0.00
43:	N-PHENYLCARBAZOLE ISO-PCI (M+H) G2=-20.3V 2.2MT ARGON 243 C18.H13.N (139, 30)(140, 30)(166, 898)	0:00 0.000 0.	0.00
44:	PALMITIC ACID ISO-PCI (M+H) G2=-20.4V 2.0MT ARGON 256 C16.H32.O2 (43, 908)(55, 189)(57, 1000)	0:00 0.000 0.	0.00
45:	OLEIC ACID ISO-PCI (M+H) G2=-20.4V 2.0MT ARGON 282 C18.H34.O2 (43, 477)(55, 522)(57, 1000)	0:00 0.000 0.	0.00
46:	PALMITIC ACID ISO+N2O-NCI (M-H) G2=+20.9V 2.2MT ARGON 256 C16.H32.O2 (83, 1)(94, 1)(237, 19)	0:00 0.000 0.	0.00
47:	BENZOIC ACID ISO+N2O-NCI (M-H) G2=+20.0V 2.2MT ARGON 122 C7.H6.O2 (77, 1000)(106, 12)(121, 203)	0:00 0.000 0.	0.00
48:	RESORCINOL ISO-PCI (M+H) G2=-20.4V 2.2MT ARGON 110 C6.H6.O2 (39, 34)(43, 5)(55, 24)	0:00 0.000 0.	0.00
49:	P-CHLORDANILINE ISO-PCI (M+H) G2=-20.1V 2.1MT ARGON 127 C6.H6.N.CL (75, 20)(92, 18)(93, 1000)	0:00 0.000 0.	0.00
50:	CHLOROBENZENE PEI (M+) G2=-20.0V 1.9MT ARGON 112 C6.H6.CL (77, 106)(111, 6)(112, 1000)	0:00 0.000 0.	0.00
51:	DIBENZOTHIOPHENE ISO-NCI (M-) G2=+19.7V 2.2MT ARGON 184 C12.H8.S (183, 1000)(184, 507)	0:00 0.000 0.	0.00

52:	4-CHLOROBENZONITRILE ISO-PCI (M+H) Q2=-20.1V 2.1MT ARGON 137 C7.H7.N.CL (75, 21)(102, 172)(111, 448)	0:00 0.000 0.	0.00
53:	BENZYL CHLORIDE PEI (M+) Q2=-20.0V 1.9MT ARGON 126 C7.H7.CL (50, 10)(90, 23)(91, 365)	0:00 0.000 0.	0.00
54:	2-CHLOROACETOPHENONE ISO-PCI (M+H) Q2=-20.1V 2.1MT ARGON 154 C8.H7.O.CL (77,1000)(91, 225)(119, 23)	0:00 0.000 0.	0.00
55:	2,5-DIMETHYLTHIOPHENE ISO-PCI (M+H) Q2=-20.0V 2.0MT ARGON 112 C6.H6.S (41, 36)(59, 21)(69, 204)	0:00 0.000 0.	0.00
56:	BROMOPHOS ISO-PCI (M+H) Q2=-20.1V 2.4MT ARGON 365 C8.H8.O3.S.CL2.P.BR (109, 305)(125,1000)(127, 16)	0:00 0.000 0.	0.00
57:	1,2,3,4-TETRAHYDROISOQUINOLINE ISO-PCI Q2=-20.0V 2.0MT ARGON 133 C9.H11.N (79, 16)(91, 25)(105, 177)	0:00 0.000 0.	0.00
58:	TRIFLUOROACETYL DERIV 1,2,3,4-TETRAHYDROISOQUINOLINE ISO-PCI (M+H) Q2= 229 C11.H10.O.N.F3 (41, 50)(107, 67)(118, 160)	0:00 0.000 0.	0.00
59:	TRIFLUOROACETYL DERIV 9-AMINOPHENANTHRENE ISO-PCI (M+H) Q2=-20.0V 2.0M 289 C16.H10.O.N.F3 (167, 60)(177, 684)(193,1000)	0:00 0.000 0.	0.00
60:	1,2,3,4-TETRAHYDROQUINOLINE ISO-PCI (M+H) Q2=-20.0V 2.0MT ARGON 133 C9.H11.N (77, 3)(79, 3)(93, 3)	0:00 0.000 0.	0.00
61:	TRIFLUOROACETYL DERIV 1,2,3,4-TETRAHYDROISOQUINOLINE ISO-PCI (M+H) Q2= 229 C11.H10.O.N.F3 (105,1000)(115, 207)(117, 694)	0:00 0.000 0.	0.00
62:	PHENOL ISO-PCI (M+H) Q2=-20.0V 2.0MT ARGON 94 C6.H6.O (41, 24)(51, 35)(57, 23)	0:00 0.000 0.	0.00
63:	ANILINE ISO-PCI (M+H) Q2=-20V 2.0MT ARGON 93 C6.H7.N (51, 27)(57, 18)(76, 18)	0:00 0.000 0.	0.00
64:	ANILINE CH3F-PCI (M+CH3) Q2=-20V 2.1MT ARGON 93 C6.H7.N (65, 10)(78, 13)(91, 46)	0:00 0.000 0.	0.00
65:	PHENOL CH3F-PCI (M+CH3) Q2=-20V 2.1MT ARGON 94 C6.H6.O (65, 35)(77, 201)(78, 16)	0:00 0.000 0.	0.00
66:	2,4,6 D3-PHENOL ISO-PCI (M+H) Q2=-20.0V 2.0MT ARGON 97 C6.H3.O.D3 (52, 17)(53, 19)(57, 36)	0:00 0.000 0.	0.00
67:	D5-PHENOL ISO-PCI (M+H) Q2=-20.0V 2.0MT ARGON 99 C6.H.O.D5 (72, 16)(81, 444)(82, 162)	0:00 0.000 0.	0.00
68:	O-TOLUIDINE ISO-PCI (M+H) Q2=-20V 2.0MT ARGON 107 C7.H9.N (39, 14)(41, 16)(65, 64)	0:00 0.000 0.	0.00
69:	P-TOLUIDINE ISO-PCI (M+H) Q2=-20V 2.0MT ARGON 107 C7.H9.N (65, 231)(90, 30)(91, 916)	0:00 0.000 0.	0.00

70:	N-METHYLANILINE ISO-PCI (M+H) Q2=-20V 2.0MT ARGON				
	107 C7.H9.N	0:00	0.000	0.	0.00
	(66, 3)(92, 4)(93, 249)				
71:	P-CRESOL ISO-PCI (M+H) Q2=-20V 2.0MT ARGON				
	108 C7.H8.O	0:00	0.000	0.	0.00
	(55, 15)(65, 165)(67, 70)				
72:	ANISOLE ISO-PCI (M+H) Q2=-20V 2.0MT ARGON				
	108 C7.H8.O	0:00	0.000	0.	0.00
	(39, 73)(51, 48)(57, 52)				
73:	O-CRESOL ISO-PCI (M+H) Q2=-20.0V 2.0MT ARGON				
	108 C7.H8.O	0:00	0.000	0.	0.00
	(65, 23)(79, 39)(80, 8)				
74:	M-METHOXYPHENOL ISO-PCI (M+H) Q2=-20.1V 2.2MT ARGON				
	124 C7.H8.O2	0:00	0.000	0.	0.00
	(65, 145)(69, 15)(77, 21)				
75:	5-HYDROXYINDOLE ISO-PCI (M+H) Q2=-20.1V 2.2MT ARGON				
	133 C8.H7.O.N	0:00	0.000	0.	0.00
	(77, 41)(79, 38)(89, 19)				
76:	ACENAPHTHYLENE ISO-PCI (M+H) Q2=-20.1V 2.2MT ARGON				
	152 C12.H8	0:00	0.000	0.	0.00
	(55, 12)(57, 7)(83, 8)				
77:	DIMETHYLNAPHTHALENE ISO-PCI (M+H) Q2=-20.1V 2.2MT ARGON				
	156 C12.H12	0:00	0.000	0.	0.00
	(91, 4)(115, 47)(125, 3)				
78:	1-NITRONAPHTHALENE ISO-PCI (M+H) Q2=-20.1V 2.2MT ARGON				
	173 C10.H7.O2.N	0:00	0.000	0.	0.00
	(77, 28)(116, 37)(117, 34)				
79:	9,10-DIHYDROPHENANTHRENE ISO-PCI (M+H) Q2=-20.1V 2.2MT ARGON				
	180 C14.H12	0:00	0.000	0.	0.00
	(57, 206)(125, 488)(139, 217)				
80:	PYRENE ISO-PCI (M+H) Q2=-20.1V 2.2MT ARGON				
	202 C16.H10	0:00	0.000	0.	0.00
	(201, 40)(202, 825)(203, 1000)				
81:	6-PHENYLQUINOLINE ISO-PCI (M+H) Q2=-20.1V 2.2MT ARGON				
	205 C15.H11.N	0:00	0.000	0.	0.00
	(77, 4)(128, 8)(152, 4)				
82:	1-AMINOPYRENE ISO-PCI (M+H) Q2=-20.1V 2.2MT ARGON				
	217 C16.H11.N	0:00	0.000	0.	0.00
	(151, 1)(165, 1)(189, 12)				
83:	CHRYSENE ISO-PCI (M+H) Q2=-20.1V 2.2MT ARGON				
	228 C18.H12	0:00	0.000	0.	0.00
	(152, 1)(200, 2)(201, 3)				
84:	TOLUENE ISO-PCI (M+H) Q2=-20V 2.0MT ARGON				
	92 C7.H8	0:00	0.000	0.	0.00
	(41, 49)(51, 188)(65, 40)				
85:	ETHYL BENZENE ISO-PCI (M+H) Q2=-20V 2.3MT ARGON				
	106 C8.H10	0:00	0.000	0.	0.00
	(65, 20)(77, 31)(79, 1000)				
86:	P-XYLENE ISO-PCI (M+H) Q2=-20V 2.0MT ARGON				
	106 C8.H10	0:00	0.000	0.	0.00
	(41, 140)(51, 20)(65, 190)				
87:	DIMETHYLPHENOL ISO-PCI (M+H) Q2=-20.0V 2.2MT ARGON				
	122 C8.H10.O	0:00	0.000	0.	0.00
	(67, 44)(77, 271)(79, 182)				
88:	THIOANISOLE ISO-PCI (M+H) Q2=-20.0V 2.2MT ARGON				
	124 C7.H8.S	0:00	0.000	0.	0.00
	(51, 11)(65, 45)(66, 26)				

89:	1-CYCLOPENTYL-1-THIABUTANE ISO-PCI (M+H) G2=-20.0V 2.2MT ARGON 144 C8.H16.S (41, 237)(42, 3)(43, 242)	0:00	0.000	0.	0.00
90:	ACENAPHTHENE ISO-PCI (M+H) G2=-20.0V 2.2MT ARGON 154 C12.H10 (77, 36)(115, 65)(127, 114)	0:00	0.000	0.	0.00
91:	1-CYCLOPENTYL-1-THIAPENTANE ISO-PCI (M+H) G2=-20.0V 2.2MT ARGON 158 C9.H18.S (41, 196)(56, 5)(57, 447)	0:00	0.000	0.	0.00
92:	2-NAPHTHALENETHIOL ISO-PCI (M+H) G2=-20.0V 2.2MT ARGON 160 C10.H8.S (77, 1)(102, 1)(116, 1)	0:00	0.000	0.	0.00
93:	DITETRAHYDROTHIOPHENE ISO-PCI (M+H) G2=-20.0V 2.2MT ARGON 174 C8.H14.S2 (41, 93)(57, 162)(69, 283)	0:00	0.000	0.	0.00
94:	ACRIDINE ISO-PCI (M+H) G2=-20.0V 2.2MT ARGON 179 C13.H9.N (151, 2)(152, 7)(153, 1)	0:00	0.000	0.	0.00
95:	4-METHYLDIBENZOTHIOPHENE ISO-PCI (M+H) G2=-20.0V 2.2MT ARGON 198 C13.H10.S (139, 2)(152, 2)(165, 1)	0:00	0.000	0.	0.00
96:	ISO-PCI (M+H) G2=-20.0V 2.2MT ARGON 200 C10.H16.S2 (41, 62)(43, 191)(56, 19)	0:00	0.000	0.	0.00
97:	FLUORANTHENE ISO-PCI (M+H) G2=-20.0V 2.2MT ARGON 202 C16.H10 (200, 2)(201, 3)(202, 457)	0:00	0.000	0.	0.00
98:	NAPHTHACENE ISO-PCI (M+H) G2=-20.0V 2.2MT ARGON 228 C18.H12 (57, 2)(202, 2)(226, 4)	0:00	0.000	0.	0.00
99:	2,4-DIPHENYLTHIOPHENE ISO-PCI (M+H) G2=-20.0V 2.2MT ARGON 236 C16.H12.S (103, 16)(115, 11)(128, 18)	0:00	0.000	0.	0.00
100:	CORONENE ISO-PCI (M+H) G2=-20.0V 2.2MT ARGON 300 C24.H12 (298, 1)(299, 2)(300, 145)	0:00	0.000	0.	0.00
101:	2,3,4-TRIPHENYLTHIOPHENE ISO-PCI (M+H) G2=-20.0V 2.2MT ARGON 312 C22.H16.S (115, 430)(141, 199)(143, 1000)	0:00	0.000	0.	0.00
102:	HYDROQUINONE ISO-PCI (M+H) G2=-20.0V 2.0MT ARGON 110 C6.H6.O2 (39, 1)(55, 10)(57, 8)	0:00	0.000	0.	0.00
103:	BENZYLAMINE ISO-PCI (M+H) G2=-20.0V 2.2MT ARGON 107 C7.H9.N (65, 44)(91, 1000)(108, 10)	0:00	0.000	0.	0.00
104:	N-BUTYLBENZENE PEI(M+) G2=-20V 2.2MT ARGON 134 C10.H14 (65, 58)(78, 30)(90, 40)	0:00	0.000	0.	0.00
105:	CUMENE ISO-PCI (M+H) G2=-20.0V 2.2MT ARGON 120 C9.H12 (41, 54)(42, 16)(43, 1000)	0:00	0.000	0.	0.00
106:	(-) CAMPHOR ISO-PCI (M+H) G2=-20.0V 2.2MT ARGON 152 C10.H16.O (43, 315)(55, 107)(67, 134)	0:00	0.000	0.	0.00
107:	1-METHYLFLUORENE ISO-PCI (M+H) G2=-20.0V 2.2MT ARGON 180 C14.H12 (121, 2)(135, 2)(141, 30)	0:00	0.000	0.	0.00

108:	9-ETHYLFLUORENE ISO-PCI (M+H) Q2=-20.0V 2.2MT ARGON 194 C15.H14 (117, 14)(152, 36)(153, 15)	0:00 0.000	0.	0.00
109:	ANTHRAQUINONE ISO-PCI (M+H) Q2=-20.0V 2.2MT ARGON 208 C14.H8.O2 (77, 1)(105, 7)(127, 1)	0:00 0.000	0.	0.00
110:	3-ETHYL-2-PENTANONE PEI (M+) Q2=-20V 0.4MT ARGON 114 C7.H14.O (43, 102)(58, 20)(68, 20)	0:00 0.000	0.	0.00
111:	3-ETHYL-2-PENTANONE PEI (M+) Q2=-20V 2.0MT ARGON 114 C7.H14.O (41, 121)(43, 1000)(53, 49)	0:00 0.000	0.	0.00
112:	N-METHYLANILINE PEI (M+) Q2=-20V 2.1MT ARGON 107 C7.H9.N (51, 20)(65, 51)(77, 717)	0:00 0.000	0.	0.00
113:	O-TOLUIDINE PEI (M+) Q2=-20V 2.1MT ARGON 107 C7.H9.N (67, 10)(77, 79)(79, 69)	0:00 0.000	0.	0.00
114:	P-HYDROXYBIPHENYL ISO-PCI (M+H) Q2=-20V 2.0MT ARGON 170 C12.H10.O (65, 39)(77, 79)(93, 40)	0:00 0.000	0.	0.00
115:	18-CROWN-6 ISO-PCI (M+H) Q2=-20V 2.0MT ARGON 264 C12.H24.O6 (45, 195)(87, 17)(89, 1000)	0:00 0.000	0.	0.00
116:	4-HYDROXYPYRIDINE ISO-PCI (M+H) Q2=-20.0V 2.1MT ARGON 95 C5.H5.O.N (39, 46)(41, 143)(43, 9)	0:00 0.000	0.	0.00
117:	4-HYDROXYPIPERIDINE ISO-PCI (M+H) Q2=-20.0V 2.1MT ARGON 101 C5.H11.O.N (41, 23)(42, 138)(53, 11)	0:00 0.000	0.	0.00
118:	3-HYDROXY-6-METHYLPYRIDINE ISO-PCI (M+H) Q2=-20.0V 2.1MT ARGON 109 C6.H7.O.N (39, 34)(41, 42)(42, 27)	0:00 0.000	0.	0.00
119:	5-HYDROXYINDOLE ISO-PCI (M+H) Q2=-20.0V 2.1MT ARGON 133 C8.H7.O.N (39, 189)(77, 201)(79, 184)	0:00 0.000	0.	0.00
120:	4-HYDROXY-2-METHYLQUINOLINE ISO-PCI (M+H) Q2=-20.0V 2.1MT ARGON 159 C10.H9.O.N (77, 44)(91, 10)(105, 4)	0:00 0.000	0.	0.00
121:	5-HYDROXYISOQUINOLINE ISO-PCI (M+H) Q2=-20.0V 2.2MT ARGON 145 C9.H7.O.N (65, 9)(77, 2)(91, 213)	0:00 0.000	0.	0.00
122:	2-DECANONE ISO-PCI (M+H) Q2=-20.0V 2.2MT ARGON 156 C10.H20.O (41, 254)(43, 132)(45, 257)	0:00 0.000	0.	0.00
123:	1,3-DIHYDROXYNAPHTHALENE ISO-PCI (M+H) Q2=-20.0V 2.2MT ARGON 160 C10.H8.O2 (55, 68)(69, 94)(77, 118)	0:00 0.000	0.	0.00
124:	9-HYDROXYFLUORENE ISO-PCI (M+H) Q2=-20.0V 2.2MT ARGON 182 C13.H10.O (43, 46)(55, 36)(57, 30)	0:00 0.000	0.	0.00
125:	9-PHENANTHROL ISO-PCI (M+H) Q2=-20.0V 2.2MT ARGON 194 C14.H10.O (39, 11)(45, 8)(141, 6)	0:00 0.000	0.	0.00
126:	4-METHOXYPHENOL ISO-PCI (M+H) Q2=-19.8V 2.1MT ARGON 124 C7.H8.O2 (65, 338)(77, 100)(81, 50)	0:00 0.000	0.	0.00

127:	PENTADIENE FROM DICYCLOPENTADIENE ISO-PCI (M+H) G2=-20V 2.0MT ARGON	0.00	0.000	0	0.00
	66 C5 H6 (39, 302)(41, 975)(45, 109)				
128:	CYCLOHEXANECARBOXAMIDE ISO-PCI (M+H) G2=-20V 2.0MT ARGON	0.00	0.000	0.	0.00
	127 C7 H13 O N (46, 309)(55, 722)(67, 198)				
129:	DICYCLOPENTADIENE ISO-PCI (M+H) G2=-20V 2.0MT ARGON	0.00	0.000	0.	0.00
	132 C10 H12 (41, 21)(55, 19)(65, 10)				
130:	TETRAMETHYLENE SULFOXIDE ISO-PCI (M+H) G2=-20V 2.0MT ARGON	0.00	0.000	0.	0.00
	104 C4 H8 O S (45, 50)(53, 10)(55, 71)				
131:	TETRAMETHYLENE SULFONE ISO-PCI (M+H) G2=-20V 2.0MT ARGON	0.00	0.000	0.	0.00
	120 C4 H8 O2 S (41, 186)(55, 673)(57, 36)				
132:	2,3-DIMETHYLCYCLOHEXYLAMINE ISO-PCI (M+H) G2=-20V 2.0MT ARGON	0.00	0.000	0.	0.00
	127 C8 H17 N (41, 336)(43, 50)(55, 598)				
133:	1,2-DIHYDRONAPHTHALENE ISO-PCI (M+H) G2=-20V 2.0MT ARGON	0.00	0.000	0.	0.00
	130 C10 H10 (53, 21)(65, 10)(91, 1000)				
134:	CYCLOOCTYLAMINE ISO-PCI (M+H) G2=-20V 2.0MT ARGON	0.00	0.000	0.	0.00
	127 C8 H17 N (41, 437)(43, 50)(55, 598)				
135:	5-AMINOVALERIC ACID ISO-PCI (M+H) G2=-20V 2.0MT ARGON	0.00	0.000	0.	0.00
	117 C5 H11 O2 N (43, 30)(55, 1000)(56, 349)				
136:	5-AMINOURACIL ISO-PCI (M+H) G2=-20V 2.0MT ARGON	0.00	0.000	0.	0.00
	127 C4 H5 O2 N3 (55, 271)(57, 20)(72, 10)				
137:	4-AMINO-2,6-DIHYDROXYPYRIDINE ISO-PCI (M+H) G2=-20.0V 2.2MT ARGON	0.00	0.000	0.	0.00
	127 C4 H5 O2 N3 (42, 73)(43, 43)(44, 19)				
138:	4-PICOLINE (4-METHYLPYRIDINE) ISO-PCI (M+H) G2=-20.0V 2.2MT ARGON	0.00	0.000	0.	0.00
	93 C6 H7 N (41, 115)(52, 10)(53, 32)				
139:	2,6-DIMETHYLPYRIDINE (2,6-LUTIDINE) PEI (M+) G2=-20V 2.0MT ARGON	0.00	0.000	0.	0.00
	107 C7 H9 N (40, 120)(42, 110)(65, 943)				
140:	2,6-DIMETHYLPYRIDINE (2,6-LUTIDINE) ISO-PCI (M+H) G2=-20V 2.0MT ARGON	0.00	0.000	0.	0.00
	107 C7 H9 N (41, 266)(42, 19)(65, 212)				
141:	METHYLHYDROQUINONE ISO-PCI (M+H) G2=-19.8V 2.1MT ARGON	0.00	0.000	0.	0.00
	124 C7 H8 O2 (77, 521)(79, 214)(81, 24)				
142:	HYDROQUINONE CH3F-PCI (M+CH3) G2=-19.8V 2.1MT ARGON	0.00	0.000	0.	0.00
	110 C6 H6 O2 (65, 20)(77, 51)(79, 34)				
143:	CATECHOL CH3F-PCI (M+CH3) G2=-19.8V 2.1MT ARGON	0.00	0.000	0.	0.00
	110 C6 H6 O2 (65, 85)(77, 406)(79, 241)				
144:	RESORCINOL CH3F-PCI (M+CH3) G2=-19.8V 2.1MT ARGON	0.00	0.000	0.	0.00
	110 C6 H6 O2 (65, 154)(77, 117)(79, 148)				

145:	3-METHYLCATECHOL ISO-PCI (M+H) Q2=-19.8V 2.1MT ARGON			
	124 C7.H8.O2	0:00	0.000	0.00
	(77, 1000)(79, 502)(107, 456)			
146:	4-METHYLCATECHOL ISO-PCI (M+H) Q2=-19.8V 2.1MT ARGON			
	124 C7.H8.O2	0:00	0.000	0.00
	(57, 23)(77, 1000)(79, 594)			
147:	GUAIACOL (O-METHOXYPHENOL) ISO-PCI (M+H) Q2=-19.8V 2.1MT ARGON			
	124 C7.H8.O2	0:00	0.000	0.00
	(65, 1000)(82, 26)(93, 474)			
148:	2-METHYLRESORCINOL ISO-PCI (M+H) Q2=-19.8V 2.1MT ARGON			
	124 C7.H8.O2	0:00	0.000	0.00
	(69, 18)(77, 338)(79, 232)			
149:	5-METHYLRESORCINOL ISO-PCI (M+H) Q2=-19.8V 2.1MT ARGON			
	124 C7.H8.O2	0:00	0.000	0.00
	(77, 238)(79, 170)(82, 33)			
150:	3-METHOXYPHENOL ISO-PCI (M+H) Q2=-19.8V 2.1MT ARGON			
	124 C7.H8.O2	0:00	0.000	0.00
	(65, 828)(77, 157)(81, 37)			
151:	CYCLOOCTANONE ISO-PCI (M+H) Q2=-20V 2.0MT ARGON			
	126 C8.H14.O	0:00	0.000	0.00
	(41, 60)(43, 111)(55, 567)			
152:	P-AMINOPHENOL ISO-PCI (M+H) Q2=-20V 2.0MT ARGON			
	109 C6.H7.O.N	0:00	0.000	0.00
	(39, 21)(57, 10)(65, 650)			
153:	M-NITROPHENOL ISO-PCI (M+H) Q2=-20V 2.0MT ARGON			
	139 C6.H5.O3.N	0:00	0.000	0.00
	(65, 389)(82, 19)(93, 1000)			
154:	4-HYDROXYQUINOLINE ISO-PCI (M+H) Q2=-20V 2.0MT ARGON			
	145 C9.H7.O.N	0:00	0.000	0.00
	(77, 11)(91, 21)(104, 30)			
155:	1-NAPHTHOL ISO-PCI (M+H) Q2=-20V 2.0MT ARGON			
	144 C10.H8.O	0:00	0.000	0.00
	(91, 29)(115, 109)(117, 318)			
156:	P-NITROBENZOIC ACID ISO-PCI (M+H) Q2=-20V 2.0MT ARGON			
	167 C7.H5.O4.N	0:00	0.000	0.00
	(51, 417)(78, 149)(92, 10)			
157:	NITROBENZENE ISO-PCI (M+H) Q2=-20V 2.0MT ARGON			
	123 C6.H5.O2.N	0:00	0.000	0.00
	(57, 20)(66, 30)(77, 1000)			