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**TRACE COMPONENT ANALYSIS OF PROCESS HYDROGEN STREAMS AT
THE WILSONVILLE ADVANCED COAL LIQUEFACTION FACILITY**

Subcontracted R&D Final Report

By
J. C. Bronfenbrenner

Work Performed Under Contract No. AC05-78OR03054

International Coal Refining Company
Allentown, Pennsylvania

Technical Information Center
Office of Scientific and Technical Information
United States Department of Energy

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	v
EXECUTIVE SUMMARY	1
INTRODUCTION	2
TRACE COMPONENT PROGRAM	5
DISCUSSION OF RESULTS	10
SRC-I Trace Component Analyses	10
EBH Trace Component Analysis	18
Diene and NO _x Concentrations	18
Trace Element Concentrations	21
Comparison of Results	21
CONCLUSIONS AND FUTURE WORK	24
LITERATURE CITED	25
APPENDIX 1--RADIAN FINAL REPORT	27

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ABSTRACT

This report summarizes subcontracted work done by the Radian Corporation to analyze trace components in process hydrogen streams at the Advanced Coal Liquefaction Facility in Wilsonville, Alabama. The data will be used to help define whether the gas streams to be treated in the hydrogen processing unit in the SRC-I Demonstration Plant will require further treatment to remove trace contaminants that could be explosive under certain conditions.

EXECUTIVE SUMMARY

This report presents results of a two-task study performed by Radian Corporation under subcontract to International Coal Refining Co. (ICRC). During ICRC's design of the 6,000-ton-per-day SRC-I coal liquefaction demonstration plant, a potential explosion hazard was uncovered in the cryogenic hydrogen processing unit (HPU). Certain trace contaminants in the gas streams handled by that unit have the potential to freeze out and concentrate in the unit's heat exchanger. These highly concentrated gas mixtures have the potential to explode when the unit is warmed up during shutdown.

Radian's role in resolving this problem was to analyze process hydrogen streams at the Wilsonville Advanced Coal Liquefaction Facility (an SRC-I pilot plant) for all trace components suspected of being explosion hazards. To do so, they had to develop special methods to measure minute (parts per billion) concentrations of two of the contaminants--butadiene and NO_x --which could not be detected by conventional methods. Methods to measure the two components at 1-ppbv concentrations were successfully developed with acceptable reproducibility.

The results of Radian's stream analyses were compared with the results of an independent study of the hazards problem conducted by Pittsburgh and Midway Coal Mining Company (P&M). The results are comparable when all the processing differences are taken into account.

When the trace contaminant measurements are compared to design limits established by a review of industry standards, it becomes apparent that the process streams to be treated by the HPU may require further treatment beyond that now planned. ICRC will use the data from this program and the data from P&M's study to define the design basis for the demonstration plant HPU.

INTRODUCTION

To reduce America's dependence on imported petroleum, the U.S. Department of Energy (DOE) initiated the solvent-refined coal (SRC-I) direct coal liquefaction project to demonstrate the technical and economic feasibility as well as environmental acceptability of SRC-I liquefaction. Under its prime contract with DOE (No. DE-AC05-78-OR0-3054), International Coal Refining Co. (ICRC) has designed a 6,000-ton-per-day plant to demonstrate the SRC-I process.

Included in the process is a cryogenic hydrogen processing unit (HPU), designed by Air Products and Chemicals, Inc. This unit recovers hydrogen from the SRC-I and LC-Finer high- and medium-pressure gas streams for recycle. Certain trace components in these gas streams have the potential to freeze out and concentrate in the HPU's cryogenic heat exchanger. When the HPU is warmed up during shutdown, these highly concentrated gas mixtures could explode.

The Pittsburgh and Midway Coal Mining Company conducted a detailed analysis of the HPU hazards, defined acceptable contaminant concentrations, and arrived at some potential solutions for removing them (Pittsburgh and Midway Coal Mining Co., 1983). In conjunction with this analysis, ICRC developed a program to define a design basis for treating the feed to the HPU, based on the actual compositions of similar streams in the Wilsonville Advanced Coal Liquefaction Facility. This 6-tpd pilot facility is operated by DOE and the Electric Power Research Institute (EPRI) in Wilsonville, Alabama.

Several components were identified as potential hazards in the streams at Wilsonville. Since the cryogenic heat exchangers freeze out and concentrate these components, even concentration levels in the parts per billion range have the potential to be hazardous. Therefore, the concentration ranges of each anticipated component had to be defined in order to determine how long the HPU can be operated between shutdowns without risking explosion hazards.

Table I lists the pertinent process hydrogen stream components and detection limits. Although existing methods could be used to detect most of these components, special methods had to be developed to measure butadiene and NO_x concentrations at the parts per billion level. To

Table I

Trace Components to Be Analyzed

Component in process hydrogen streams	Detection limit
H ₂ S	1 ppm
COS	1 ppm
CS ₂	1 ppm
Mercaptans (CH ₃ SH, C ₂ H ₅ SH)	1 ppm
Thiophene (CH ₃ and benzyl)	1 ppm
NH ₃	100 ppm
HCl	100 ppm
HCN	1 ppm
NO _x	1 ppb ^a
Butadiene	1 ppb ^a
Trace elements	µg/m ³
Hg	0.004
Be	0.04
F (fluorocarbons)	0.9
As	0.3
Ph	0.2

^aMethod to be developed.

develop such methods, ICRC subcontracted with the Radian Corporation in Austin, Texas (Subcontract No. 01-13162). In addition to the methods development, Radian was to sample hydrogen streams from the Wilsonville plant and measure the components identified in Table I.

Radian completed the methods development task in March 1983 and the sampling at Wilsonville on May 7-10, 1983. The final report on this subcontracted program was issued in July 1983 and is included as Appendix 1 to this report.

In summary, this program had two specific objectives:

- (1) To provide analytical methods to measure parts per billion levels of NO_x and butadiene.
- (2) To analyze Wilsonville off-gas streams for the trace components listed in Table I.

The accomplishment of both these objectives forms an integral part of the resolution of Category 1 comments No.'s 3 and 4 from DOE's First Milestone Review of the HPU design.

TRACE COMPONENT PROGRAM

Radian was awarded a two-task program to develop methods for measuring parts per billion concentrations of butadiene and NO_x in process hydrogen streams and to analyze the process hydrogen streams in Wilsonville's SRC-I and ebullated bed hydrotreating coal liquefaction process units.

The procedures and validation for the methods development task are detailed in Section 3 of Radian's final report, included as Appendix 1 in this report. In summary, the methods developed can detect 1,3-butadiene to 1 ppbv. The coefficient of variation [$\% \text{ cv} = (\sigma/\bar{x}) \times 100$] for replicate samples is $<5\%$. For NO_x , the detection limit is 1 ppbv, and the coefficient of variation is 11%.

The process hydrogen streams analyzed in the Wilsonville plant are listed in Table II and identified on the process flow diagrams in Figures 1 and 2. Streams 4 and 5 were low-pressure gas streams, which will end up in the fuel gas in the SRC-I Demonstration Plant. Stream 5 was not sampled at Wilsonville because the flow is intermittent and V-161 pressure is maintained with N_2 . Analysis of this stream would not produce relevant results, since N_2 will not be present in the SRC-I Demonstration Plant. Streams 3 and 4 were sampled as a combined stream, but hindsight indicates that stream 4 was mostly N_2 . Therefore, the composition of stream 3 can be estimated by removing the N_2 and normalizing the remaining components to 100%.

The Wilsonville plant was being operated in the integrated two-stage liquefaction (ITSL) mode when the process hydrogen streams were analyzed for this study. This mode of operation differs significantly from the SRC-I Demonstration Plant process flow. (For a detailed description of the ITSL process, see the Wilsonville Technical Progress Report, July 1983.) The differences between the ITSL and SRC-I operating modes will have the following effects on trace element concentrations:

- ° Because the ITSL coal feed rate is one-third the SRC-I coal rate, at equivalent hydrogen recycle rates, the trace element concentrations measured by Radian are probably lower (assuming the trace elements came from the coal).

Table II

Plan for Sampling and Analysis at the
Wilsonville Pilot Plant

Streams to be analyzed	
1. High-pressure vent separator (V-104) overhead 1,150 psi, 80°F	
2. Water scrubber (V-106) overhead 1,150 psi, 80°F	
3. Solvent decanter (V-105) vent 10 psi, 100°F	} Sampled at point where these two streams are combined
4. Solvent column (T-104) flare 10 psi, 100°F	
5. T-105 EBH solvent column reflux tank (V-161) flare 5 psi	} Eliminated. Intermittent flows
6. Hydrotreater recycle gas (T-1059 inlet) 3-5 psi, 110°F	
7. Hydrotreater vent gas (T-1059 outlet) 3-5 psi, 110°F	

Figure 1
Wilsonville SRC Plant.
High- and Low-Pressure Gas Loops.
Material Balance May 8, 1983

88

- ° Illinois No. 6 coal was used at Wilsonville, instead of Kentucky No. 9 as planned for the demonstration plant. Although the effect on trace components is not known, it is not expected to be significant.
- ° The concentration of the trace components is a function of the ratio of net gas to recycle gas. The net/recycle gas ratio is significantly higher at Wilsonville than that for the SRC-I plant design. This means the measured concentration of trace components is lower than that expected for the SRC-I design.

Other processing differences are minor, except for the expanded-bed hydrotreater (EBH) (LC-Finer equivalent) net gas (streams 6 and 7). The sample taken at Wilsonville includes both low- and high-pressure gases. In the SRC-I design, the low-pressure gas goes to fuel. The EBH caustic scrubber also was not operated during the run, resulting in high nitrogen and sulfur compound concentrations in stream 7, which are not expected in the SRC-I LC-Finer design after caustic and water wash.

In addition, at the demonstration plant, SRC and EBH low-pressure gases are treated first by water wash and then by DEA absorption before passing to fuel gas. This should provide the necessary removal of sulfur and nitrogen compounds from the low-pressure gases. Wilsonville data for these streams were obtained from untreated gases.

DISCUSSION OF RESULTS

The analytical procedures used to determine stream composition and trace component concentrations are defined in Sections 3 and 4 of the Radian final report (Appendix 1).

All oxygen in the Radian sample analyses was assumed to come from air contamination of the samples and analytical apparatus, and the stream compositions were adjusted for this. The adjustment brought the hydrogen and nitrogen compositions into close agreement with results from Wilsonville's own analyses, giving credence to the trace component measurements (see Table III). Material balances and process conditions for the SRC and EBH hydrotreaters on the Radian sampling days are presented in Figures 1 and 2. Detailed composition data are summarized from the Radian report in Tables IV-VIII. Where components could not be detected (ND), the detection limit is shown in parentheses.

The ethylene concentration includes acetylene, if any was present. P&M reported that, in their SRC-II pilot unit, no acetylene was detected with an analytical limit of 10 ppm. C_2 through C_6 concentrations include olefins. The unidentified sulfur compounds include thiophenes (methyl-, benzyl-, and tetrahydro-) and higher mercaptans. HCN includes cyanide, as well as thiocyanate.

SRC-I Trace Component Analyses

A comparison of streams 1 and 2 (Tables IV and V) shows that caustic and water washing removed all sulfur compounds completely, except for COS, where only 90% was removed. Ninety percent of the HCN was also removed.

There was no NH_3 and only 0.5% H_2S in stream 1 (before caustic and water wash). Since the amount of nitrogen and sulfur removed from the coal and assumed converted to NH_3 and H_2S is considerably greater than the nitrogen and sulfur compounds measured, it is assumed the unaccounted NH_3 and H_2S combined into a soluble salt in E-103, which was removed in the wash water leaving V-105. A total material balance was not done on the wash water, but the composition shown in Table IX supports this analysis.

Streams 3 and 4 (Table VI) were sampled together. Since T-104 pressure is maintained with N_2 at 5-10 psi above the bubble point of the

Table III

Comparison of Radian and Wilsonville Process Gas Analyses

		Radian	Wilsonville
Stream 2:	vol % H ₂	83.8	82.2
	vol % N ₂	0.4	0.3
	MW	5.6	5.3
Stream 3:	wt % H ₂	3.3	2.7
	MW	21.5	22.4
Stream 6: ^a	vol % H ₂	96.5	96.3
	MW	3.1	2.7

^aTable X normalized to zero N₂.

Table IV
Composition and Trace Components for Wilsonville Stream 1
(SRC Process Gas from V-1040H), May 8, 1983^a

Comp	Units	MW	Concentration		lb/hr	scfh
			Volume	Weight		
H ₂	%	2	82.2	27.0	12.8	2,444
C ₁	%	16	9.8	25.8	12.2	291
C ₂ H ₄	%	28	0.029	0.13	0.1	-
C ₂ H ₆	%	30	3.3	16.3	7.7	98
C ₃	%	44	1.5	10.8	5.2	45
C ₄	%	58	0.41	3.9	1.9	12
C ₅	%	72	0.09	1.1	0.5	3
C ₆	%	86	0.06	0.85	0.4	2
N ₂	%	28	0.71	3.3	1.6	21
CO	%	28	0.9	4.1	2.0	28
CO ₂	%	44	0.38	2.8	1.3	11
H ₂ S	%	37	0.65	4.0	1.9	19
CH ₃ SH	ppm	48	24	190		
CH ₃ CH ₂ SH	ppm	62	7	72		
COS	ppm	60	5	46		
CS ₂	ppm	76	0.2	2		
SO ₂	ppm	64	ND (1.0)	ND (10.5)		
Undefined S	ppm	62	6	60		
HCN	ppm	27	6.5	29		
NH ₃	ppm	17	ND (5)	ND (14)		
HCl	ppm	36.5	ND (5)	ND (25)		
NO	ppb	30	1	5		
Total NO _x	ppb	30	12	59		
Butadiene	ppb	54	6	53		
			μg/m ³	ppb	ppb	
F		19	ND (2.2)	ND	ND	
Hg		200	2.3	0.26	7.4	
Be		9	ND (0.75)	ND	ND	
As		75	0.18	0.05	0.6	
Pb		207	ND (0.15)	ND	ND	
Total stream		6.08	100	100	47.7	2,973

^aNote: Numbers in parentheses are detectable limits. ND is not determined.

Table V
Composition and Trace Components for Wilsonville Stream 2
[Net SRC High-Pressure Process Gas (V-106 Vent)], May 8, 1983^a

Comp	Units	MW	Concentration		lb/hr	scfh
			Volume	Weight		
H ₂	%	2	83.8	30.1	3.7	702
C ₁	%	16	9.7	27.9	3.4	81
C ₂ H ₄	%	28	0.026	0.1	-	-
C ₂ H ₆	%	30	3.2	17.3	2.1	27
C ₃	%	44	1.5	11.9	1.5	13
C ₄	%	58	0.39	4.1	0.5	3
C ₅	%	72	0.08	1.0	0.2	1
C ₆	%	86	0.08	1.2	0.2	1
N ₂	%	28	0.38	1.9	0.2	3
CO	%	28	0.85	4.3	0.5	7
CO ₂	%	44	0.02	0.2	-	-
H ₂ S	%	37	ND (0.1)	ND (0.7)		
CH ₃ SH	ppm	48	ND (1.5)	ND (11)		
CH ₃ CH ₂ SH	ppm	62	ND (1.0)	ND (11)		
COS	ppm	60	0.46	5.0		
CS ₂	ppm	76	ND (0.15)	ND (2)		
SO ₂	ppm	64	ND (1.0)	ND (12)		
Undefined S	ppm	62	ND (1.0)	ND (11)		
HCN	ppm	27	0.6	2.9		
NH ₃	ppm	17	ND (5)	ND (15)		
HCl	ppm	36.5	ND (5)	ND (33)		
NO	ppb	30	24	129		
Total NO _x	ppb	30	30	162		
Butadiene	ppb	54	4	39		
			μg/m ³	ppb	ppb	
F		19	ND (1.6)	ND	ND	
Hg		200	1.5	0.17	6.0	
Be		9	0.085	0.21	0.34	
As		75	0.29	0.09	1.2	
Pb		207	ND (0.17)	ND	ND	
Total stream		5.56	100	100	12.3	838

^aNote: Numbers in parentheses are detectable limits. ND is not determined.

Table VI
Composition and Trace Components for Wilsonville Streams 3 and 4
[Net SRC Low-Pressure Process Gas (V-105 & T-104)], May 7, 1983^a

Comp	Units	MW	Concentration		lb/hr	scfh
			Volume	Weight		
H ₂	%	2	35.2	3.3	0.7	125
C ₁	%	16	7.6	5.6	1.1	27
C ₂ H ₄	%	28	0.033	0.04	-	-
C ₂ H ₆	%	30	6.3	8.8	1.8	22
C ₃	%	44	6.2	12.7	2.6	22
C ₄	%	58	3.5	9.4	1.9	12
C ₅	%	72	1.3	4.4	0.9	5
C ₆	%	86	0.87	3.5	0.7	3
N ₂	%	28	34.9	45.4	9.1	123
CO	%	28	0.21	0.3	-	1
CO ₂	%	44	0.46	0.9	0.2	2
H ₂ S	%	37	3.3	5.7	1.1	12
CH ₃ SH	ppm	48	540	1,204		
CH ₃ CH ₂ SH	ppm	62	260	749		
COS	ppm	60	34	54		
CS ₂	ppm	76	ND (0.15)	ND (0.5)		
SO ₂	ppm	64	ND (1.0)	ND (3.0)		
Undefined S	ppm	62	230	662		
HCN	ppm	27	1.7	2.1		
NH ₃	ppm	17	800	632		
HCl	ppm	36.5	ND (5)	ND (8.5)		
NO	ppb	30	61	85		
Total NO _x	ppb	30	66	92		
Butadiene	ppb	54	81	136		
			µg/m ³	ppb	µpb	
F		19	4.0	4.7	4.2	
Hg		200	12.2	1.4	12.7	
Be		9	ND (0.11)	ND	ND	
As		75	0.34	0.10	0.35	
Pb		207	ND (0.22)	0.02	0.23	
Total stream		21.5	100	100	20.1	354

^aNote: Numbers in parentheses are detectable limits. ND is not determined.

Table VII
Composition and Trace Components for Wilsonville Stream 6
(EBH Hydrotreater Process Gas to T-1059), May 9, 1983^a

Comp	Units	MW	Concentration		lb/hr	scfh
			Volume	Weight		
H ₂	%	2	86.9	31.8	0.86	
C ₁	%	16	1.18	3.4	0.09	
C ₂ H ₄	%	28	ND (0.01)	-	-	
C ₂ H ₆	%	30	0.70	3.8	0.10	
C ₃	%	44	0.39	3.1	0.08	
C ₄	%	58	0.13	1.4	0.04	
C ₅	%	72	0.05	0.7	0.02	
C ₆	%	86	0.16	2.5	0.07	
N ₂	%	28	9.6	49.2	1.33	
CO	%	28	ND (0.1)	-	-	
CO ₂	%	44	ND (0.01)	-	-	
H ₂ S	%	37	0.39	2.6	0.07	
CH ₃ SH	ppm	48	5	44	-	
CH ₃ CH ₂ SH	ppm	62	ND (1)	-	-	
COS	ppm	60	ND (0.3)	-	-	
CS ₂	ppm	76	ND (0.15)	-	-	
SO ₂	ppm	64	ND (1)	-	-	
Undefined S	ppm	62	ND (1)	-	-	
HCN	ppm	27	0.6	3	-	
NH ₃	ppm	17	4,900	15,200	0.04	
HCl	ppm	36.5	ND (5)	-	-	
NO	ppb	30	3	16	-	
Total NO _x	ppb	30	<12	66	-	
Butadiene	ppb	54	2	20	-	
			μg/m ³	ppb	ppb	
F		19	1.4	1.6	6	
Hg		200	2.5	0.3	10	
Be		9	1.5	3.7	6	
As		75	5.6	1.7	23	
Pb		207	ND (0.18)	ND	ND	
Total stream		5.47	100	100	2.7	187

^aNote: Numbers in parentheses are detectable limits. ND is not determined.

Table VIII
Composition and Trace Components for Wilsonville Stream 7
(EBH Flare Gas from T-1059), May 9, 1983^a

Comp	Units	MW	Concentration		lb/hr	scfh
			Volume	Weight		
H ₂	%	2	87.4	32.1	0.87	
C ₁	%	16	1.18	3.5	0.09	
C ₂ H ₄	%	28	ND (0.01)	-	-	
C ₂ H ₆	%	30	0.70	3.9	0.10	
C ₃	%	44	0.39	3.1	0.08	
C ₄	%	58	0.13	1.4	0.04	
C ₅	%	72	0.05	0.7	0.02	
C ₆	%	86	0.16	2.5	0.07	
N ₂	%	28	9.6	49.4	1.33	
CO	%	28	ND (0.1)	-	-	
CO ₂	%	44	ND (0.01)	-	-	
H ₂ S	%	37	0.39	2.6	0.07	
CH ₃ SH	ppm	48	5	44	-	
CH ₃ CH ₂ SH	ppm	62	ND (1)	-	-	
COS	ppm	60	ND (0.3)	-	-	
CS ₂	ppm	76	ND (0.15)	-	-	
SO ₂	ppm	64	ND (1)	-	-	
Undefined S	ppm	62	ND (1)	-	-	
HCN	ppm	27	1	5	-	
NH ₃	ppm	17	2,600	8,100	0.02	
HCl	ppm	36.5	ND (5)	-	-	
NO	ppb	30	7	-	-	
Total NO _x	ppb	30	-	-	-	
Butadiene	ppb	54	3	-	-	
			μg/m ³	pph	ppb	
F		19	9.0	10.6	37	
Hg		200	0.5	0.06	2	
Be		9	1.0	2.5	4	
As		75	4.8	1.4	20	
Pb		207	ND (0.16)	ND	ND	
Total stream		5.44	100	100	2.7	187

^aNote: Numbers in parentheses are detectable limits. ND is not determined.

Table IX
Wilsonville Wash Water Analyses
May 1, 1983

	<u>Sour water analyses (µg/L)</u>	
	SRC	EBH
Total organic carbon	20,800	2,650
Ammonia (as nitrogen)	11,900	10,850
Sulfide (as sulfur)	8,279	9,714
Chlorides	-	13
Oil and grease	1,231	160
Phenols	8,625	2,225
Inorganic carbon	-	79
Kjeldahl nitrogen	-	13,020

reflux, it can be assumed all N_2 in the stream 3 and 4 analysis is from stream 4, and all other components are from stream 3. Stream 3 has very high sulfur and nitrogen component concentrations and will require cleanup (i.e., DEA unit) before it is sent to the fuel system.

EBH Component Analysis

No caustic or water is currently used in the T-1059 caustic scrubber. Comparison of the compositions of streams 6 and 7 (in and out of the caustic scrubber) verifies that nothing was removed in T-1059 (Tables VII and VIII). It can be assumed that caustic and water washing will accomplish the same removal of sulfur and nitrogen components as seen in the SRC analyses of streams 1 and 2.

The EBH catalyst appears to convert all sulfur and most of the nitrogen compounds to H_2S and NH_3 , respectively. The level of NH_3 measured in streams 6 and 7 is very high when compared to the SRC process, but this corresponds to the high N removal from the feed SRC. Still, less than 10% of the nitrogen removed appears as NH_3 in the net process gas. Again, it is assumed that most NH_3 and H_2S combine into soluble salts in E-1213 and are removed in the wash water from V-1233. A sour water analysis supports this conclusion (Table IX).

The N_2 in streams 6 and 7 was not expected and is not normal for the hydrotreater at Wilconville. During the sampling period for streams 6 and 7, on May 9-10, 1983, the hydrogen makeup compressor (C-1205) failed. The feed was pulled and nitrogen was added to the recycle gas to maintain pressure until C-1205 was restarted. The N_2 in streams 6 and 7 is the residual left from this upset. Table X provides results of analysis of stream 6 with the N_2 removed and normalized to 100%. As can be seen in Table III, this brings the Radian analysis of stream 6 into agreement with the Wilconville analysis.

Diene and NO_x Concentrations

During the methods development task, Radian measured the diene and NO_x composition of the process gas streams several times. The results are documented in Tables 3-6 and 3-10 of the Radian final report (Appendix 1). Table XI summarizes the variation in diene and NO_x levels for each stream with multiple samples. It is clear that the measurements

Table X
Composition and Trace Components for Normalized Wilsonville Stream 6
(EBH Process Gas to T-1059 with N₂ Removed), May 9, 1983

Comp	Units	MW	Concentration		lb/hr	scfh
			Volume ^b	Weight		
H ₂	%	2	96.5	62.4		
C ₁	%	16	1.3	6.7		
C ₂ H ₄	%	28	ND (0.01)	ND (0.09)		
C ₂ H ₆	%	30	0.78	7.6		
C ₃	%	44	0.43	6.1		
C ₄	%	58	0.14	2.6		
C ₅	%	72	0.06	1.4		
C ₆	%	86	0.18	5.0		
N ₂	%	28	0.0 ^b	-		
CO	%	28	ND (0.1)	ND (0.9)		
CO ₂	%	44	ND (0.01)	ND (0.14)		
H ₂ S	%	37	0.43	5.2		
CH ₃ SH	ppm	48	5.4	84		
CH ₃ CH ₂ SH	ppm	62	ND (1.0)	ND (20)		
COS	ppm	60	ND (0.3)	ND (5.8)		
CS ₂	ppm	76	ND (0.15)	ND (3.7)		
SO ₂	ppm	64	ND (1.0)	ND (21)		
Undefined S	ppm	62	ND (1.0)	ND (20)		
HCN	ppm	27	0.7	6.1		
NH ₃	ppm	17	5,440	29,900		
HCl	ppm	36.5	ND (5)	ND (59)		
NO	ppb	30	3	29		
Total NO _x	ppb	30	13	126		
Butadiene	ppb	54	2	35		
			μg/m ³	ppb		
F		19	1.4	1.6	9.8	
Hg		200	2.5	0.3	19.4	
Be		9	1.5	3.7	10.8	
As		75	5.6	1.7	41.2	
Pb		207	ND (0.18)	ND (0.02)	ND (1.3)	
Total stream		3.09	100	100	2.7	

^aNote: Numbers in parentheses are detectable limits. ND is not determined.
^bN₂ deleted and normalized to 100%.

Table XI

Variation in Diene and NO_x Analyses
of Wilsonville Process Gas Streams

Stream no.	No. of samples	Concentration (ppbv)		
		Diene	NO	NO _x
1	4	<1 to 30	<1 to 30	<12 to 30
2	3	2 to 18	14 to 34	18 to 45
3 and 4	2	81, 170	3, 64	51, 140
6	3	<1 to 150	2 to 39	<12 to 4,600
7	2	3, 3	3, 10	-

taken during the May sampling period are a factor of 10 lower than those of January and February. The design basis must make allowance for this variation.

Trace Element Concentrations

Table XII compares the amount of trace elements in coal and solvent feeds that end up in the process gases. The amount of each trace element in the gas streams is from 2 to 5 orders of magnitude smaller than the amount in coal and solvent feeds. The concentration of the trace elements is shown in Tables IV-VIII for each stream. These are provided to evaluate materials of construction in the HPU heat exchangers.

Comparison of Results

Table XIII compares the trace component analyses of the P&M P-99 SRC-II process development unit (PDU) with the results from the SRC-I and EBH process units at Wilsonville. The P-99 SRC-II process stream was not caustic- and water-washed, and the results are comparable to the SRC-I process data before caustic and water wash. The EBH data show significantly lower amounts of all trace components except H_2S and NH_3 . This is apparently the result of the catalyst reducing almost all sulfur and nitrogen species to H_2S and NH_3 , respectively.

Since there are no major differences between the SRC-I and SRC-II process data, it can be assumed that they represent a typical range of trace component concentrations that will be in the high-pressure process hydrogen.

When these data are compared to the P&M design limits developed for the HPU, it is clear that further cleanup must be accomplished. However, a comparison of SRC-I streams 1 and 2 (Tables IV and V) shows that caustic and water wash removes almost all sulfur and nitrogen species, reducing the trace component cleanup load significantly, and leaving only NO_x and dienes for further processing.

Table XII

Comparison of Trace Elements in Coal and Solvent to
Trace Elements in Process Gas

Trace elements	$\mu\text{g/g MF}^a$ coal				
	Coal	Solvent	Strm 2	Strm 3 and 4	Strm 6
Mercury (Hg)	0.14	0.15	0.0014	0.0010	0.0001
Beryllium (Be)	<0.25	<0.28	ND	ND	0.0001
Arsenic (As)	2.2	<0.1	ND	2.8×10^{-5}	0.0002
Lead (Pb)	5	19	0.0001	1.8×10^{-5}	ND
Fluorine (fluorocarbons)	<5	<5	ND	0.0003	0.0001

^aMF, moisture free.

Table XIII

Comparison of Trace Component Concentrations in
SRC-II, SRC-I, and EBH Process Hydrogen Streams

	P&M design limits	Measured concentrations		
		P&M SRC-II P-99 PDU	Wilsonville	
			SRC-I Strm 1 (Table IV)	EBH Strm 6 (Table VII)
Hydrocarbons (ppmw)				
C ₅ ⁺	200	30,000	22,000	32,000
C ₂ -C ₄ olefins	-	9,800	<300 (C ₂ ²⁻ only)	<100 (C ₂ ²⁻ only)
Butadiene	-	-	<0.01	0.02
Acetylenes	ND ^a	ND	ND	ND
Sulfur compounds (ppmv)				
H ₂ S	1	6,200	6,500	3,900
COS	1	41	5	<0.3
CS ₂	1	1	0.2	<0.15
SO ₂	1	7	<1	<1
CH ₃ SH	1	14	24	5
C ₂ H ₅ SH	1	12	7	<1
Other S	1	1	6	<1
Nitrogen compounds (ppmv)				
NH ₃	1	30	<5	4,900
NO	0.004	0.020	0.01	0.003
NO ₂		1	0.01	0.010
Oxygen compounds (ppmv)				
CO ₂	5	1,600	3,800	<0.01
CO	ND	5,800	9,000	<0.1
O ₂	ND	ND	ND	ND
H ₂ O	1	750	ND	ND
Other (ppmv)				
HCl	1	2	<5	<5
HCN	1	2	6.5	0.6
HF	1	ND	<0.018	0.016

^aND, not determined.

CONCLUSIONS AND FUTURE WORK

The results of this program for the SRC-I and EBH processes and those published by P&M Coal Mining Co. for the SRC-II process (shown in Table XIII) are comparable when all of the processing differences are taken into account. When the measurements are compared to the design limits set by P&M's review of industry standards, it is apparent that some treating beyond standard water and caustic washing may be required.

The following conclusions can be drawn from the results of this subcontracted program:

- The methods developed for measuring butadiene and NO_x in SRC process hydrogen streams achieved 1-ppbv detection limits and gave acceptable reproducibility.
- The butadiene and NO_x concentrations have been observed to vary by an order of magnitude in most streams (10-100 ppbv).
- The low-pressure gas streams from the SRC unit (3 and 4) and from the EBH unit will require removal of sulfur and nitrogen compounds before being sent to the fuel system. At the demonstration plant, the DEA unit is designed to perform this function.
- Compared with design limits developed by P&M for the HPU feed gas, the Wilsonville high-pressure gas streams would require additional cleanup beyond caustic and water wash for removal of NO_x and dienes. The demonstration plant concentrations of trace contaminants are expected to be higher than those measured during the test runs, because:
 - (a) Wilsonville was being operated in the integrated two-stage liquefaction mode.
 - (b) The net gas-to-recycle gas ratio at Wilsonville was higher, due to the high purge gas rate used at Wilsonville.

- ° Because of the wide measured variations (10-100 ppbv) in NO_x and butadiene, the demonstration plant design must be based on the higher values until additional data have been generated to isolate the cause and extent of the variations. (Additional sample analysis at Wilsonville, by others, would be recommended.) Evaluation of the impact of the test measurements on the SRC-I Baseline Design is currently in progress, and will be reported separately.

ICRC will evaluate these data and those generated by P&M to define a design basis for treating the process gas streams prior to entering the HPU cryogenic heat exchangers.

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Appendix 1

Radian Corporation Final Report

TRACE CONTAMINANTS ANALYSIS
OF GASEOUS STREAMS AT THE
ADVANCED TWO-STAGE COAL LIQUEFACTION
RESEARCH UNIT
IN WILSONVILLE, ALABAMA

Final Report

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ABSTRACT

Trace impurities in gas streams will have a profound effect on the process design of the gas treating and sulfur recovery units for coal conversion facilities. Also, the presence of certain trace impurities may lead to severe corrosion and/or environmental pollution. Identification and quantification of these trace contaminants is needed to evaluate their potential impact on the SRC Demonstration Plant process design.

The two gas streams of interest are the high pressure H_2 recycle gas and low pressure fuel gas. Trace contaminants in the high pressure H_2 loop pose two problems: (1) an explosion hazard in the Hydrogen Purification Unit due to accumulation of NO_x and unsaturated di-olefins and (2) potential freezeout of some sulfur species. Trace contaminants in the low pressure fuel gas pose both a corrosion problem and an environmental problem since this stream will ultimately be combusted.

A two-phase program has been completed to provide data for addressing these concerns in the Demonstration Plant process design:

Phase I - Analytical techniques were developed to detect NO_x and butadiene at concentrations approaching one part per billion in gas samples from the Wilsonville SRC Pilot Plant.

Phase II - Sampling and analysis of five gas streams at the Wilsonville Pilot Plant was performed for major gases (CO , CO_2 , H_2 , O_2 , N_2), hydrocarbons (C_1 - C_6), sulfur species (H_2S , CO_2S , CS_2 , mercaptans), nitrogen species (NH_3 , HCN , NO_x), chloride, fluoride, and trace elements (Hg, Be, As, Pb).

This report documents the results of the program that was carried out in the December, 1982 - June, 1983 time period.

CONTENTS

<u>Section</u>	<u>Page</u>
1 INTRODUCTION	1-1
Background	1-1
Scope of Work	1-2
Report Organization	1-2
2 SUMMARY OF RESULTS AND CONCLUSIONS	2-1
Methods Development Results	2-1
Sampling and Analysis Results	2-2
Conclusions	2-8
Recommendations	2-10
3 METHODS DEVELOPMENT	3-1
Butadiene Method Development	3-1
NO _x Method Development	3-17
4 DESCRIPTION OF SAMPLING AND ANALYSIS METHODOLOGY	4-1
Sampling	4-1
Analysis Methodology	4-12
5 REFERENCES	5-1
APPENDIX A COMPARISON OF ON-SITE AND OFF-SITE GAS ANALYSES	A-1

ILLUSTRATIONS

<u>Figure</u>	<u>Page</u>
3-1 Experimental Approach for Developing Diene Methodology	3-3
3-2 Schematic Diagram of the Diene Analytical System	3-6
3-3 Linearity Study for Diene Analytical System	3-11
3-4 Chromatographic Analysis of Process Gas From Vent V104 With and Without Butadiene Spike (Sample Collected 2/16/83 and Analyzed 2/28/83)	3-15
3-5 Schematic Diagram of the NO _x Analytical System	3-22
3-6 Linearity of Nitric Oxide (NO) and Nitrogen Dioxide (NO ₂)	3-26
3-7 Analysis of Sample V104 Overhead Vent With and Without Nitric Oxide Spike	3-29
3-8 NO _x Calibration Results for Field Sampling	3-36
4-1 Day 1 Sample Collection Schedule	4-2
4-2 Day 2 Sample Collection Schedule	4-3
4-3 Day 3 Sample Collection Schedule	4-4
4-4 SRC Flowsheet	4-6
4-5 Hydrotreater Flowsheet	4-7
4-6 Schematic of the Gas Sampling Manifold System	4-9
4-7 Complete Gas Sampling System	4-11
4-8 Preparation and Metals Analysis	4-16

TABLES

<u>Table</u>		<u>Page</u>
2-1	Gas Streams Sampled at the Wilsonville, Alabama Pilot Plant	2-3
2-2	Summary Analytical Results of Coal Liquefaction Pilot Plant Gas Streams - Wilsonville, Alabama Facility	2-4
2-3	Summary Analytical Results of Coal Liquefaction Pilot Plant Gas Streams - Wilsonville, Alabama Facility	2-6
2-4	Analytical Results of Process Coal and Solvent - Wilsonville, Alabama Facility	2-9
3-1	Compounds Tested for Interferences in the Diene Method	3-10
3-2	Replicability of 1,3-Butadiene Determinations	3-13
3-3	Results of Replicability Study of V104 Sample	3-14
3-4	Butadiene Spiking Study Results	3-16
3-5	Results of Butadiene Stability Study of V104 Sample	3-18
3-6	Summary of Analytical Results for Butadiene	3-19
3-7	Replicability of Nitric Oxide and Nitrogen Dioxide Determinations	3-27
3-8	Results of Stability Study for NO in Tedlar® Bags	3-30
3-9	Results of Stability Study for NO _x in Tedlar® Sampling Bags	3-31
3-10	Summary of Analytical Results for NO and NO _x	3-33
3-11	Summary of Field Calibration Results for NO (May 6-8, 1983)	3-34
3-12	Summary of Field Calibration Results for NO (May 9, 1983)	3-35
3-13	Statistical Analysis of NO Field Data	3-37
4-1	Analysis Methods for Impinger Solutions	4-13

Section 1

INTRODUCTION

Under International Coal Refining Company Subcontract No. 01-13162 Radian Corporation determined the level of trace components in gaseous streams from the SRC Pilot Plant in Wilsonville, Alabama. Although previous testing has been performed for major components in gaseous streams from coal liquefaction facilities, very limited data has been obtained for trace impurities. The latter may have a profound effect on process design of gas treating and sulfur receiving units. In addition the presence of certain trace impurities may lead to severe corrosion and/or environmental pollution.

Identification and quantification of trace contaminants were performed to provide ICRC with a basis for evaluating the potential impact on the commercial-scale plant design for a coal liquefaction facility. In addition major components were also quantified to provide background or reference conditions for process gas streams. The test work was performed during the period of May 7-9, 1983 when the Wilsonville Pilot Plant was being operated on an eastern coal feedstock (Illinois #6 from the Burning Star Mine).

BACKGROUND

ICRC under contract to the Department of Energy (DOE) is preparing a commercial-scale plant design for a coal liquefaction facility. Part of the design has resulted from considering the Pilot Plant design operation at the advanced two-stage liquefaction research unit in Wilsonville, Alabama. The Pilot Plant which is sponsored by the U.S. Department of Energy (DOE) and the Electric Power Research Institute (EPRI) is managed by Southern Company Services (SCS). Catalytic, Inc. provides the day-to-day operating manpower and maintenance personnel.

Radian initiated work on the Trace Contaminant Analysis project in December 1982. Adequate methods for the testing were not available for all of the components of interest to ICRC. Radian's experience in complex component gaseous streams indicated that method research would be required to select analytical techniques for the analysis of a reactive organic component (1,3-butadiene) and of NO_x at concentrations approaching 1 ppbv. Accumulation of these species in the Hydrogen Purification Unit for a commercial facility can pose an explosion hazard. Therefore the program included method development for these two components prior to a field effort to collect gas stream data.

SCOPE OF WORK

The scope of work consisted of two phases. Phase one consisted of development of the analytical capability to detect 1,3-butadiene and NO_x at concentrations approaching 1 ppbv in hydrocarbon-laden gas streams. Samples of gas streams obtained from the Wilsonville facility were used along with prepared standards.

In the second phase Radian supplied equipment and personnel at the Wilsonville SRC Pilot Plant to conduct a gas characterization program. Analyses were conducted on five gas streams for the following components: H_2S , COS, CS_2 , mercaptans, thiophene, SO_2 , NH_3 , HCl, HCN, NO_x , 1,3-butadiene, Hg, Be, F, As, Pb. To verify the integrity of gas samples requiring off-site analysis, analyses were to be conducted by gas chromatography for major components such as H_2 , N_2 , CO and $\text{C}_1\text{-C}_5$ hydrocarbons at Wilsonville before shipping and at the laboratory in Austin upon receipt. Coal and process solvent samples were characterized for Hg, Be, F, As, and Pb.

REPORT ORGANIZATION

This report documents the activities performed under the Scope of Work (previous section). Section 2 presents a summary of results of the method

development phase and the sampling and analysis phase of the program. Conclusions are presented addressing the methods, results and problems encountered. A description of the butadiene and NO_x methods developed in phase one is found in Section 3. The sampling and analysis methodology is described in Section 4. References to chemical analysis methodology are listed in Section 5. A comparison of on-site and off-site analyses is presented in Appendix A.

Section 2

SUMMARY OF RESULTS AND CONCLUSIONS

Radian selected, developed and tested methods for analysis of 1,3-butadiene and NO_x to validate their applicability to process gas streams from the Wilsonville Pilot Plant. Radian also performed sampling and on-site analysis of gaseous streams at the Wilsonville facility during the period of May 7-9, 1983. The results of both efforts are presented as well as conclusions concerning the data obtained.

METHODS DEVELOPMENT RESULTS

Methods were developed to determine 1,3-butadiene, NO and NO_x in the hydrogen streams. These methods are described in detail in Section 3. All methods had detection limits of approximately 1 ppbv, precision on standards of approximately 10% and precision on Wilsonville samples of better than 30%. The linearity of the methods was excellent. Recovery studies demonstrated good accuracy for the sample matrices. A number of potential interferences were checked and none proved to be an actual interference.

Butadiene was determined by gas chromatography using subambient isothermal temperature conditions, cryogenic concentration and focusing, and photoionization detection using a 9.5 eV ionization source. The method provided selectivity of approximately 10^6 over other C_4 alkanes and alkenes. Samples for butadiene were collected in stainless steel canisters and transported to the laboratory for analysis. A storage time of 7 days was shown to be adequate before significant sample degradation took place.

The methods developed for NO_x species in the complex hydrogen stream involved cryogenic concentration, gas chromatographic separation of NO from

other sample components, and detection by chemiluminescence reaction with ozone. Total NO_x was determined by first passing the sample gas through a heated catalyst to reduce NO_x species to NO. The ozone reaction is very sensitive and selective for NO, but has several interferences which were present in the sample gas. Gas chromatography was used in conjunction with the ozone reaction to remove NO from other interferences. Samples for NO_x were collected in light-shielded Tedlar® bags and analyzed within 4 hours.

SAMPLING AND ANALYSIS RESULTS

Table 2-1 lists the gas streams which were sampled at the Wilsonville facility during the period of May 7-9, 1983. Raw coal and process solvent were also obtained for trace element analysis.

Gas Stream Results

Summary results for major components, C_1 - C_6 hydrocarbons, and trace sulfur species for the five process gaseous streams are presented in Table 2-2. (All gas stream results were corrected for possible air contamination during sample collection. The oxygen content of samples was determined. Both oxygen and the corresponding nitrogen equivalent of air were subtracted from raw sample results. All other gas values were then corrected for air except hydrogen. Hydrogen was determined by difference. Air contributions to the raw sample results ranged from 0.5 to 4.0 percent.) Hydrogen was the major component (82-87 percent) of four of the five streams; the V105/T104 combined vent stream was 35 percent hydrogen. Nitrogen was detected at less than one percent in the V104 and V106 high pressure hydrogen recycle streams, at 9-10 percent in the T1059 hydrotreater gases and at 35 percent in the V105/T104 combined vent stream.

The V104 and V106 high pressure hydrogen recycle streams contained 15 percent hydrocarbons in the C_1 through C_6 series; methane at a concentration of 10 percent was the major hydrocarbon specie. The T1059 hydrotreater gases contained 2-3 percent C_1 - C_6 hydrocarbons; primarily as methane, ethane

Table 2-1

GAS STREAMS SAMPLED AT THE WILSONVILLE, ALABAMA PILOT PLANT

<u>Stream</u>	<u>Stream ID</u>	<u>Description/Location</u>
1	H.P. Vent Separator Gas (V104 Overhead)	High pressure hydrogen recycle gas exiting the vent separator V104 vessel.
2	Water Scrubber Gas (V106 Overhead)	High pressure hydrogen recycle gas after caustic and water scrubbing collected from the overhead of the V106 water scrubber.
3 and 4	Combined Stream 3 - Solvent decanter (V105) vent 4 - Fractionating column (T104) flare gas	Vent gas from the solvent decanter (V105) and flare gas from the fractionating column (T104) after they are combined as a common stream to the flare.
6	Hydrotreater Recycle Gas (T1059 Inlet)	A combination of vent streams from the hydrotreater unit including flash vessels, reflux tank and excess recycle gas sampled at the inlet to the T1059 scrubber.
7	Hydrotreater Vent (T1059 Outlet)	Vent gas from T1059 scrubber which is sent to the flare.

Table 2-2

SUMMARY ANALYTICAL RESULTS OF COAL LIQUEFACTION PILOT PLANT
GAS STREAMS - WILSONVILLE, ALABAMA FACILITY

Component, Concentration Units	1 H.P. Vent Separator (V104 Overhead)	2 Water Scrubber (V106 Overhead)	3/4 Solvent Decanter/ Column Vents (V105/T104)	6 Hydrotreater Recycle (T1059 Inlet)	7 Hydrotreater Vent (T1059 Outlet)
H ₂ , % ¹	82.2	83.3	35.2	86.9	87.4
CO, %	0.90±0.37 ²	0.85±0.34	0.21±0.06	ND (0.1) ³	ND (0.1)
CO ₂ , %	0.38±0.10	0.02±0.02	0.46±0.00	ND (0.01)	ND (0.01)
N ₂ , %	0.71±0.50	0.38±0.27	34.9±5.1	9.5±1.8	9.9±2.4
C ₁ , %	9.8±0.6	9.7±1.0	7.6±1.1	1.18±0.04	0.89±0.01
C ₂ (Ethylene), %	0.029±0.001	0.025±0.007	0.033±0.005	ND (0.01)	ND (0.01)
C ₂ (Ethane), %	3.3±0.2	3.2±0.2	6.3±0.8	0.70±0.01	0.55±0.04
C ₃ , %	1.5±0.1	1.5±0.0	6.2±0.3	0.39±0.02	0.31±0.03
C ₄ , %	0.41±0.04	0.33±0.04	3.5±0.5	0.13±0.00	0.11±0.01
C ₅ , %	0.09±0.01	0.03±0.00	1.3±0.3	0.05	0.04±0.00
C ₆ , %	0.06±0.06	0.03±0.02	0.87±0.04	0.16±0.06	0.20±0.09
H ₂ S, %	0.65±0.32	ND (0.1)	3.3±0.3	0.39±0.01	0.31±0.02
CH ₃ SH, ppmv	24.1±0.3	ND (1.5)	540±1	4.9±2.9	ND (1.5)
CH ₃ CH ₂ SH, ppmv	7.1±1.2	ND (1.0)	260±4	ND (1.0)	ND (1.0)
COS, ppmv	4.7±2.8	0.46±0.06	34±7	ND (0.3)	ND (0.3)
CS ₂ , ppmv	0.16±0.21	ND (0.15)	ND (0.15)	ND (0.15)	ND (0.15)
SO ₂ , ppmv	ND (1.0)	ND (1.0)	ND (1.0)	ND (1.0)	ND (1.0)
Unidentified S Compounds, ppmv ⁴	5.9±7.3	ND (1.0)	230±6	ND (1.0)	ND (1.0)

¹Determined by difference.

²x±y = mean ± standard deviation.

³ND () = Not detected (detection limit).

⁴As CH₃CH₂SH.

and C₃. The V105/T104 combined vent gas contained 26 percent C₁-C₆ hydrocarbons, primarily methane, ethane, C₃ and C₄.

The V104 high pressure hydrogen recycle stream contained 0.65 percent H₂S with trace levels of methyl mercaptan, ethyl mercaptan, carbonyl sulfide and carbon disulfide. The caustic scrubber was effective in removing H₂S and reduced sulfur species in the V106 scrubber overhead gas to "less than" (nondetectable) levels. The T1059 inlet gas contained 0.39 percent H₂S and approximately 5 ppmv methyl mercaptan. After cleaning in a scrubber (which did not have caustic addition) the T1059 outlet gas still contained H₂S at the 0.31 percent level. Scrubbing with caustic should effectively remove the reduced sulfur species from the T1059 stream as observed for the V106 gas.

The V105/T104 combined vent gas contained the highest sulfur levels: 3.3 percent H₂S, 540 ppmv methyl mercaptan, 260 ppmv ethyl mercaptan, 34 ppmv carbonyl sulfide, and 230 ppmv unidentified sulfur compounds (quantitated as ethyl mercaptan).

Although thiophene was not detected at the 5 ppmv level in any of the process streams, the presence of thiophene derivatives cannot be ruled out in the V105/T104 combined vent since unidentified sulfur compounds were observed.

Additional trace component results from Table 2-3 show hydrogen cyanide at low ppmv levels in all five streams. A comparison of the hydrogen recycle streams (V104 and V106) showed that the caustic scrubber removed a majority of the hydrogen cyanide from the hydrogen recycle gas.

Ammonia was not detected in the V104 and V106 hydrogen recycle gases. However, concentrations of 800 and 4900 ppmv were observed in the V105/T104 combined vent gas and the hydrotreater recycle gas (T1059 inlet), respectively. After scrubbing the ammonia content of the T1059 outlet gas was approximately 50 percent lower than the inlet.

TABLE 2-3

SUMMARY ANALYTICAL RESULTS OF COAL LIQUEFACTION PILOT PLANT
GAS STREAMS - WILSONVILLE, ALABAMA FACILITY

Component, Concentration Units	1 H.P. Vent Separator (V104 Overhead)	2 Water Scrubber (V106 Overhead)	3/4 Solvent Decanter/ Column Vents (V105/T104)	6 Hydrotreater Recycle (T1059 Inlet)	7 Hydrotreater Vent (T1059 Outlet)
HCN, ppmv	6.5±5.4 ¹	0.6±0.5	1.7±0.5	0.6±0.2	1.2±1.2
NH ₃ , ppmv	ND (5) ²	ND (5)	800±70	4900±700	2600±300
HCl, ppmv	ND (5)	ND (5)	ND (5)	ND (5)	ND (5)
F, µg/M ³	ND (2.2)	ND (1.6)	4.0 (1.0) ³	1.4 (1.4)	9.0 (3.0)
Hg, µg/M ³	2.3±1.2	1.5±1.0	12.2±4.3	2.5±0.3	0.5±0.5
Be, µg/M ³	ND (0.075)	0.085 (0.035)	ND (0.11)	1.5	1.0
As, µg/M ³	0.18 (0.15)	0.29 (0.17)	0.34 (0.22)	5.5	4.8
Pb, µg/M ³	ND (0.15)	ND (0.17)	ND (0.22)	ND (0.13)	ND (0.16)
Diene, ppbv	6±7	4±3	8.1	2±2	3±0.2
NO _x , ppbv	<12	30±17	66±21	<12	--4
NO, ppbv	<1	24±14	61±4	3±1	7±5

¹x±y = mean ± standard deviation.

²ND () = Not detected (detection limit).

³x () = Analytical result (detection limit).

⁴-- = Instrument catalyst contamination--No NO_x result.

Hydrogen chloride (HCl) was not detected in the gas streams at the 5 ppmv level. However fluoride was observed in the hydrotreater gases (T1059) in the range of 1.4 to 9.0 $\mu\text{g}/\text{M}^3$ (corresponding to 2 to 10 ppbv). Fluoride was also detected in this range (4 $\mu\text{g}/\text{M}^3$ = 5 ppbv) in the V105/T104 combined vent gas stream.

Mercury was detected at levels in the range of 0.5-2.5 $\mu\text{g}/\text{M}^3$ for the V104 and V106 hydrogen recycle gases and the T1059 inlet and outlet gases. The V105/T104 combined vent gas contained mercury at a concentration of 12.2 $\mu\text{g}/\text{M}^3$.

Beryllium was at or below detectable levels (approximately 0.1 $\mu\text{g}/\text{M}^3$) in 3 of the 5 streams. The beryllium levels of the T1059 inlet and outlet gases were 1.5 and 1.0 $\mu\text{g}/\text{M}^3$, respectively.

Arsenic was detected in all five gas streams. The levels were 0.2-0.3 $\mu\text{g}/\text{M}^3$ in the V104 and V106 hydrogen recycle streams and the V105/T104 combined vent streams; 5-6 $\mu\text{g}/\text{M}^3$ of arsenic was observed in the T1059 inlet and outlet streams.

Lead was not detected at approximately the 0.2 $\mu\text{g}/\text{M}^3$ level in any gas streams.

Butadiene levels were 2 to 6 ppbv for all streams except the V105/T104 combined vent stream where 81 ppbv was observed.

NO and NO_x results were in fairly good agreement indicating a majority of the NO_x is present as NO. The V105/T104 combined vent stream had the highest level (61 ppbv NO and 66 ppbv NO_x). NO determination using the cryogenic trap indicated average stream levels of <1 to 7 ppbv for V104 and V106 hydrogen recycle gases and the T1059 inlet and outlet gases. The levels (24 ppbv NO and 30 ppbv NO_x) in the scrubbed hydrogen recycle (V106) stream were higher than those before scrubbing. Sufficient process data are not available to Radian to evaluate these results after scrubbing with those for the gas before scrubbing.

The gas samples were also characterized offsite for fixed gases and C₁-C₆ hydrocarbons to define sample stability in the stainless steel canisters used for storage prior to off-site analysis. Very little difference in results was noticed between on-site and off-site results indicating no major sample degradation. Appendix A contains a comparison of on-site and off-site analyses.

Coal and Process Solvent Results

Trace element results for the raw coal and process solvent are listed in Table 2-4. Mercury was detected at equivalent levels in the coal and process solvent (approximately 0.15 µg/g). Arsenic although detected in the coal was not observed in the solvent. Arsenic was observed in the hydrotreater recycle gas and hydrotreater vent gas.

The lead content of the solvent is roughly three times higher than that of the coal. Also, lead was undetected in any process gas streams.

Neither beryllium or fluoride was found in the coal or solvent at the detection levels listed in Table 2-4.

CONCLUSIONS

- The methods developed for butadiene and NO_x achieved necessary detection levels and gave reproducible results. High recoveries of components spiked into the process samples indicated the methods were applicable to the complex gas matrix.
- Variability in results for butadiene and NO_x was observed for samples from different Wilsonville plant runs. Specifically, the butadiene levels of streams and NO_x levels of two streams (V104 and 1059 inlet) were higher in samples collected by plant personnel in January and February (and shipped to Radian) than for samples collected in the May Radian sampling effort. There is insufficient information available to determine whether the variability is a function of process operation or collection procedures.
- The combined vent (V105/T104) will require treatment prior to either combustion or venting based upon the levels of reduced sulfur compounds.

Table 2-4

ANALYTICAL RESULTS OF PROCESS COAL AND SOLVENT - WILSONVILLE, ALABAMA FACILITY

<u>TE</u> ¹	<u>Coal</u> <u>(Composite 1)</u> ²	<u>Coal</u> <u>(Composite 2)</u> ³	<u>Solvent</u> <u>(Composite 1)</u> ⁴	<u>Solvent</u> <u>(Composite 2)</u> ⁵
Hg	0.14	0.15	0.16	0.14
Be	<0.28	<0.20	<0.34	<0.23
As	2.6	1.8	<0.1	<0.1
Pb	5	6	19	18
F	<5	<5	<5	<5

¹Concentration in $\mu\text{g/g}$ (ppm) on a dry weight basis.

²Composite of 2 coal samples: 5/7/83 1700 hrs, 5/8/83 1930 hrs.

³Composite of 2 coal samples: 5/9/83 day shift, 5/9/83 1820 hrs.

⁴Composite of 2 solvent samples from V131B: 5/7/83 1700 hrs, 5/8/83 1930 hrs.

⁵Composite of 2 solvent samples from V131B: 5/9/83 day shift, 5/9/83 1835 hrs.

RECOMMENDATIONS

Based upon the results of the trace analysis program Radian recommends that the following program activities be initiated.

Due to the high variability of samples taken in January, February and May, additional gas samples from V104, V106, and T1059 inlet should be characterized for NO_x and butadiene. These streams should also be analyzed for fixed gases and $\text{C}_1\text{-C}_6$ hydrocarbons to document the gas sample matrix and any major changes from the May test results and matrices.

The NO_x analysis should be performed onsite again since sample stability has indicated a maximum NO_x degradation of approximately 10 percent over a 4-hour period.

Section 3

METHODS DEVELOPMENT

A major portion of the project effort involved developing analytical techniques for determining 1,3-butadiene and oxides of nitrogen (NO_x) species at levels approaching 1 ppbv in high pressure hydrogen recycle gas streams. Accumulation of these species in the Hydrogen Purification Unit can pose an explosion hazard. Analytical techniques for these gaseous species were successfully developed with detection limits approaching 1 ppbv. These techniques were then used to analyze five gas streams at the Wilsonville Demonstration Plant. Results of the methods development, validation and application are presented in this section.

The following samples were collected by plant personnel and shipped to Radian for use in the methods development phase of the program:

- H.P. vent separator (V104 overhead) gas, 1-14-83;
- Solvent decanter (V105) vent, 1-14-83;
- Hydrotreater recycle (T1059 inlet) gas, 1-14-83; and
- H.P. vent separator (V104 overhead) gas, 2-16-83.

BUTADIENE METHOD DEVELOPMENT

The first objective of the methods development task was to develop a method to determine dienes at concentrations approaching 1 ppbv in highly complex gas streams. To simplify the problem of detecting all dienes present in the gas streams, 1,3-butadiene (referenced as butadiene for simplicity) was chosen as a model compound. This compound was a good candidate because of the high levels of 1-butenes which are present in the gas streams. The

primary difficulty in determining butadiene at the 1 ppbv level in the gas streams is that other C₄ compounds were present in percent levels. This required a differentiation factor of 10⁵ to 10⁷ for compounds with boiling points that only differ by several degrees.

Experimental Approach

Radian's approach to determining butadiene at the required detection level in the complex H₂ recycle gas stream consisted of three steps, as outlined in Figure 3-1. The first step involved separation of butadiene from the H₂ matrix and concentration of this species to provide the appropriate detection levels. The second step involved separation of butadiene from other hydrocarbon species and the third involved detection and quantitation of butadiene. The experimentation involved in evaluating each of these steps is described briefly in this section. Following establishment of the ultimate method to be used, considerable work was performed to validate this method on both standard gases and gas streams from the Wilsonville facility. Validation data are presented in later sections.

Matrix Separation and Concentration. A cryogenic concentration (CC) apparatus for separating hydrocarbons from other gases and concentrating the hydrocarbons was developed and evaluated at Radian prior to initiation of this project. The CC apparatus was previously evaluated for butadiene and could provide the necessary concentrations for sub-ppbv level detection of this species in ambient air. The hydrogen matrix presents no problems to the CC apparatus. No modifications or developmental work was required for this step of the analysis.

Separation of Butadiene from Other Hydrocarbons. The focal point of developing a method to measure butadiene in the H₂ recycle gas stream was differentiation of this species from other hydrocarbons collected during the cryogenic concentration step. Several gas chromatographic columns were identified to have the potential of separating C₄ dienes from other hydrocarbons. The columns that were evaluated are:

Figure 3-1. Experimental Approach for Developing Diene Methodology

1. 0.19% picric acid on Carbopak B, packed column;
2. VZ-10;
3. 15% EDO-1 on Chromasorb PAW;
4. DB-5 capillary column.

Each column was evaluated for ability to separate butadiene from other hydrocarbon species. In addition to comparing the different columns, column length, packing, and temperature programming were optimized for each column. A 20" x 1/8" o.d. stainless steel column packed with 15% EDO-1 on Chromasorb PAW was chosen for this method. This column provided the best separation of butadiene from other sample components. A 2" x 1/8" o.d. stainless steel column packed with Poropak Q was placed between the analytical column and detector to reduce bleed to the detector. The column system was operated isothermally at -20°C.

Detection and Quantitation of Butadiene. Detection and quantitation of butadiene were accomplished with a photoionization detector (PID). The PID responds to compounds based on ionization potentials. As a general rule, ionization potentials decrease as the degree of unsaturation in a compound increases. By carefully choosing the energy of the ionization source used with the PID, it was possible to differentiate various chemical classes based on degree of unsaturation. A 9.5 ev ionization source was used for this method. This source provided complete selectivity of butadiene over C₄ and C₅ alkanes, and provided partial selectivity of butadiene over mono-olefins and mercaptans.

Method Portability. Initial attempts were directed toward developing a simple column system which could be transported to the ICRC facility (during Phase II). However, the nature of butadiene and complexity of the problem required subambient temperature programming. The instrumentation used to provide the subambient temperature programming was too large and sensitive to be transported in a mobile laboratory. Off-site analysis involved finding an appropriate sample container and performing storage stability studies.

Hardware Description

A schematic diagram of the analytical system developed for diene determinations is presented in Figure 3-2. The system was designed to allow analysis of a variety of sample volumes. Small sample volumes (0.5 to 5.0 mL) were analyzed by syringe injections. Larger sample volumes were drawn through the cryogenic trap into an evacuated reservoir. The volume of gas passed through the cryogenic trap was calculated by monitoring the pressure change in the reservoir with a high-precision vacuum gauge (Wallace and Tiernan Model 61C-1A-0015). The sample first passed through a Tenax pretrap where heavy hydrocarbons were removed. After injection of the sample, the pretrap was flushed with 1 L of ultrahigh purity (UHP) grade N₂ to ensure complete recovery of the diene from the pretrap. Sample components were then flushed onto a glass bead-packed cryogenic trap. Organic compounds were separated from the H₂ matrix and concentrated on a 6" x 1/8" o.d. nickel tube packed with 80/100 mesh glass beads and cooled in liquid oxygen (-183°C). Trap loading and injection flows were controlled by a two-position eight-port valve (Valco No. V-8-HTa). The valve and associated stainless steel connecting tubing were heated to 60°C to avoid sample condensation. Organic species were rapidly desorbed by immersing the trap in boiling water until the temperature of the trap reached 90°C. At that time (approximately 20 s), the water bath was removed and the trap was heated to 180°C with a 750-W heating cartridge (Watlow No. J4A198). Trap temperatures were controlled with an Omega Model 4201 RTD temperature controller. Desorbed compounds were swept from the trap to the chromatographic column by He carrier gas. The transfer lines to the column were heat traced (60°C) 1/16" o.d. stainless steel tubing.

The gas chromatograph used was a Varian 3700 GC with subambient temperature programming capabilities. The detector used was a HNU Model 52 high-temperature PID. A Varian Vista 401 Chromatographic Data System was used for processing of raw chromatographic data.

Figure 3-2. Schematic Diagram of the Diene Analytical System

Procedures

The analysis procedure involved warming up the PID for one hour, cooling the column oven to -20°C , instrument calibration, and sample analysis. All calibrations and analyses were performed isothermally at -20°C . Analyses were performed by cooling the cryogenic trap in a Dewar of liquid oxygen, applying an appropriate volume of sample or standard and purging the Tenax pretrap with 1 L of UHP nitrogen. The cryogenic trap was then rapidly heated and the eight-port valve was switched to the analyze position. The butadiene peak eluted in about 13 minutes.

Calibrations were performed using a 640 ppbv standard of 1,3-butadiene in nitrogen. This standard was obtained through dilution of a 10 ppmv standard of butadiene obtained from Scott Environmental. Small volumes (0-10 mL) of standard or sample were measured with a precision gas-tight syringe. Larger volumes (10-50 mL) were measured by monitoring the pressure difference of the evacuated reservoir. Calibrations were performed prior to sample analysis and intermittently between sample analyses. A response factor was calculated based on instrument response to a given volume of butadiene using the following relations:

$$\text{Sample Volume: } V_s = \frac{P_2 - P_1}{14.7} V_r$$

where:

P_2 = final reservoir pressure (psia)

P_1 = initial reservoir pressure (psia)

V_r = reservoir volume (L)

The response factor was calculated as:

$$\text{Response Factor: } RF = \frac{A_s}{C_s V_s}$$

where:

RF = area/nL butadiene

A_S = average integrated area of standard peak

C_S = concentration of standard (ppbv = nL/L)

V_S = volume of standard analyzed (L)

Samples were analyzed exactly as standards. Butadiene concentrations in samples were calculated from the peak area using the following equation:

$$\text{Butadiene Concentration: } C_B = \frac{A_B}{RF V_G}$$

where:

C_B = concentration of butadiene (ppbv)

A_B = area of butadiene peak

R_F = response factor (area/nL)

V_G = volume of sample analyzed (L)

The butadiene peak was identified by retention time in all cases. For some samples containing very low concentrations of butadiene, it was not possible to obtain accurate electronic integration of the butadiene peak due to tailing of the methyl mercaptan peak preceding it. In these cases, the peak height was measured manually and compared to peak heights of standards using the equations presented above and substituting peak height for area.

Method Validation

A considerable amount of method validation work was performed to assure specificity of the method, and to define the analytical detection limit, precision, accuracy, linearity, and storage stability. Results of the method validation work are summarized in this section.

Specificity. During the column evaluation, a number of hydrocarbons and mercaptans were evaluated for potential interferences. The compounds tested are summarized in Table 3-1. None of these compounds produced interferences by coeluting with butadiene. Methyl mercaptan eluted one minute before butadiene and produced a tailing peak. When large amounts of methyl mercaptan were present with respect to butadiene, the tailing did carry over to the butadiene peak. This sometimes resulted in integration errors and required manual peak evaluation.

The method specificity was also evaluated by spiking samples with butadiene. In all cases, the butadiene peak in the unspiked sample coincided with the butadiene spike.

Linearity and Detection Limits. Butadiene standards were prepared by dilution of a commercially available, ppm-level 1,3-butadiene standard. For the linearity study a diluted standard of 640 ppbv-butadiene was used. Amounts of the diene analyzed were varied by injecting different volumes of this standard.

Figure 3-3 plots the linearity of this method. The left vertical axis represents the absolute quantities in nanoliters of butadiene analyzed. The right axis represents the concentration of butadiene assuming a representative sample volume of 100 mL. The bottom axis represents the integrated area of the standard peak. Linearity was good through this concentration range, yielding a correlation coefficient of 0.9983. The lowest amount of butadiene analyzed was 0.32 nL, which corresponds to a 3.2 ppbv concentration given a 100 mL sample volume. This is the smallest amount of butadiene that could be accurately injected given a standard of 640 ppbv-butadiene. The integrated area obtained at this level was greater than the minimum area for the method by a factor of five. Therefore, a detection limit approaching 1 ppbv is achievable with a sample volume of 100 mL.

Table 3-1

COMPOUNDS TESTED FOR INTERFERENCES IN THE DIENE METHOD

Methane	1-Butene	n-Pentane
Ethane	Isobutene	1-Pentene
Ethylene	c-2-Butene	c-2-Pentene
Propane	t-2-Butene	t-2-Pentene
Propylene	1-Butyne	Methyl mercaptan
Isobutane	Neopentane	Ethyl mercaptan
n-Butane	Isopentane	n-Butyl mercaptan

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Figure 3-3. Linearity Study for Diene Analytical System

Replicability. A standard butadiene gas sample of 640 ppbv butadiene was used to test the method replicability. Levels of butadiene were varied by analyzing different volumes of this standard. Table 3-2 presents replicability data obtained for multiple analyses of standards. The levels of diene tested ranged from approximately 0.3 nL to approximately 16 nL. Replicabilities were excellent at the middle concentrations, the coefficient of variation being less than 1%. Results were good at the extremes also, the coefficient of variation being less than 10%.

To determine method replicability on the actual sample matrix, the February V104 gas sample was analyzed in triplicate. Results from this study are presented in Table 3-3. The overall coefficient of variation (CV) was 11.3%, only slightly higher than the CV for the low concentration standard.

Accuracy and Applicability. Figure 3-4 shows chromatograms of the analysis of the V104 process gas sample with and without a spike of butadiene. This sample contained 9.1 ppbv-butadiene when analyzed on 2-28-83. The sample was analyzed a second time with a spike of 7.4 nL-butadiene. Analysis results showed 108% recovery of the spike. There was a definite amount of "tailing" that occurs from the peak eluting earlier than butadiene. Spike studies were also performed on samples collected during May. A summary of all spike results is presented in Table 3-4. For five spike experiments, recoveries ranged from 76% to 108% with a mean recovery of $93\% \pm 13\%$. These results demonstrate that the method was very efficient at determining butadiene in the sample matrix.

Storage Stability. Samples were collected in evacuated stainless steel canisters and shipped to Radian's Austin laboratories for analysis. Since a time delay existed between sample collection and analysis, studies were performed to determine the stability of butadiene in stainless steel canisters. Initial studies were performed with an artificial mixture of ppb levels of butadiene and ppm levels of NO_x in hydrogen. No degradation of butadiene was observed over a 0-4 day period under these conditions. Stability studies were also performed on actual samples.

Table 3-2
REPLICABILITY OF 1,3-BUTADIENE DETERMINATIONS

<u>Number of Analyses</u>	<u>Volume of Standard Analyzed (mL)¹</u>	<u>Calculated Quantity of Butadiene Analyzed (nL)</u>	<u>Replicability (% CV)²</u>	<u>Pooled CV (% CV)</u>
3	0.5	0.32	8.4	
3	5.0	3.19	0.3	
3	15.0	9.58	0.8	
3	25.0	15.96	4.7	4.8

¹640 ppbv-butadiene standard.

²% CV = Percent Coefficient of Variation

$$= \frac{SD}{Mean} \times 100\%$$

Table 3-3
RESULTS OF REPLICABILITY STUDY OF V104 SAMPLE¹

<u>Analysis Number</u>	<u>Sample Volume (mL)</u>	<u>Measured Diene Concentration (ppbv)</u>
1	50	16.2
2	50	14.7
3	50	<u>18.2</u>
Mean:		16.4
% CV: ²		10.8

¹Sample collected on 2/16/83 and analyzed on 2/23/83.

²CV = Coefficient of Variation = relative std. deviation =

$$\frac{\text{std. deviation}}{\text{mean}} \times 100\%$$

Figure 3-4. Chromatographic Analysis of Process Gas From Vent V104 With and Without Butadiene Spike (Sample Collected 2/16/83 and Analyzed 2/28/83)

Table 3-4

BUTADIENE SPIKING STUDY RESULTS

<u>Sample Stream</u>	<u>Collection Date</u>	<u>Sample Volume (mL)</u>	<u>Butadiene Spike (nL)</u>	<u>Expected Spike Concentration (ppbv)</u>	<u>Recovery (%)</u>
V104	2/16/83	100	7.4	74	108
V105/T104	5/8/83	10	1.75	175	76.4
T1059	5/9/83	50	0.583	11.7	99.5
V105/T104	5/8/83	10	0.583	58.3	82.4
T1059	5/9/83	50	0.583	11.7	98.7

The V104 gas sample, collected by Wilsonville personnel in February and shipped immediately to Austin for analysis, was analyzed three times over a span of four to twelve days after collection. The results of this study are presented in Table 3-5. The concentration of butadiene did not change between the fourth and seventh day after collection, but a significant reduction was noticed upon analysis twelve days after collection. Radian therefore recommended that butadiene samples be collected in stainless steel canisters and that analysis be performed as soon as possible (and not later than one week) after collection to ensure accurate results.

Application Results

The method developed for diene determinations was applied to samples collected during three time periods. One set of samples was collected during January, 1983 and analyzed approximately one month later. A single sample was collected in February and analyzed within four days. The extensive sample effort occurred during May, 1983. In this case, duplicate samples were collected within several hours. Results for all analyses are presented in Table 3-6. The results are arranged by stream to illustrate variations observed during different sampling periods.

In general, samples collected during January, 1983 contained greater amounts of butadiene. The cases where this was significant were sample streams V105 and T1059. Results obtained for stream V105 during May, 1983 also included stream T104 since the two streams had been combined. Since Radian does not have information concerning plant operations during January and May, it is not possible to make any conclusions concerning differences in butadiene concentrations in these streams. Further sampling of these streams is recommended.

NO_x METHOD DEVELOPMENT

The second methods development task was to develop a method to detect oxides of nitrogen (NO_x) species at concentrations down to 1 ppbv in complex hydrogen gas streams. Initial work was directed at determining NO and NO₂

Table 3-5
RESULTS OF BUTADIENE STABILITY STUDY OF V104 SAMPLE¹

<u>Analysis Date</u>	<u>Days After Collection</u>	<u>Sample Volume (mL)</u>	<u>Butadiene Concentration (ppbv)</u>
2/20/83	4	50	15.6
2/23/83	7	50	16.4 ²
2/28/83	12	100	9.1

¹Sample collected on 2/16/83.

²Mean value of triplicate determinations (16.2, 14.7 and 18.2 ppbv).

Table 3-6
SUMMARY OF ANALYTICAL RESULTS FOR BUTADIENE

<u>Sample Stream</u>	<u>Collection Date</u>	<u>Analysis Date</u>	<u>Butadiene Concentration (ppbv)</u>
V104	1/14/83	2/16/83	30
	2/16/83	2/20/83	16
	5/8/83	5/16/83	<1
	5/8/83	5/18/83	11
V105	1/14/83	2/15/83	170
V105/T104	5/7/83	5/18/83	8.1
V106	1/14/83	2/16/83	18
	5/8/83	5/16/83	1.8
	5/8/83	5/18/83	6.7
T1059 Inlet	1/14/83	2/15/83	150
	5/9/83	5/16/83	<1
	5/9/83	5/18/83	2.9
T1059 Outlet	5/9/83	5/16/83	3.0
	5/9/83	5/18/83	3.3

separately. However, because of the complexity of the hydrogen streams, only NO was determined separately and NO_x was determined as the sum of all reactive nitrogen oxide species.

Experimental Approach

The method developed for determining oxides of nitrogen (NO_x) species, nitric oxide (NO) and nitrogen dioxide (NO₂), at levels approaching 1 ppbv in the process streams involved using an oxides-of-nitrogen (NO_x) analyzer and chromatographically separating NO from the other stream components. The NO_x analyzer is based on the gas phase chemiluminescence reaction between nitric oxide and ozone. Nitrogen dioxide can also be determined by passing the gas stream through a catalytic reduction chamber, reducing NO₂ to NO, and determining total NO plus NO₂. This analyzer is considered selective for NO and NO₂ in ambient air. However, in process gas streams, other components which might also produce a chemiluminescence reaction with ozone may be present at high concentrations. Some of the primary interferences with the chemiluminescent reaction are ethylene and gaseous sulfur species. Also, some organic nitro-compounds will degrade to produce NO when passed through the catalytic reduction chamber. In addition, NO_x analyzers are generally only sensitive to about 5 to 10 ppb.

To overcome the selectivity and sensitivity problems, the experimental method involved cryogenic concentration and separation of NO from the hydrogen matrix, and chromatographic separation of NO from the other components in the gas stream. The NO_x analyzer served as the gas chromatographic detector, and NO was detected as a peak with a chromatographic integrator. Initially, it was intended to directly determine NO₂ from the column effluent. However, this compound did not chromatograph well; its retention time was so long that it could not be separated sufficiently from the bulk of the gas stream hydrocarbon interferences. To determine NO₂, the gas stream samples were routed through a catalytic converter to convert NO₂ to NO and then cryogenically concentrated. Each sample was analyzed at least twice, once for NO and once for NO plus NO₂. This method was not the most selective

for NO_2 , since some organic nitro compounds could produce a signal. However, with the complexity of the sample, it was considered to be the best possible approach.

Three columns were evaluated for separating NO from other process gas components. The three columns are listed below:

1. 10 ft. x 1/8 in. Poropak QS (80/100) Teflon,
2. 16 ft. x 1/8 in. Porasil B (80/100) Teflon, and
3. 6 ft. x 1/8 in. Carbopak B (60/80) Teflon.

The Carbopak B column did not provide good recoveries of NO . Both the Poropak QS and Porasil B columns initially gave good response for NO . The Poropak QS column packing is composed of an organic polymer (polystyrene-divinylbenzene copolymer). Organic column packings such as this can undergo chemical reactions with oxides of nitrogen. After a period of time, the NO response obtained from this column began to decrease, indicating that there was a reaction of this nature taking place. The Porasil B column which is inorganic in nature gave consistent, high responses for NO . Therefore, this column was chosen for extensive testing.

Hardware Description

A schematic diagram of the apparatus developed to determine NO_x is presented in Figure 3-5. A 3-way valve was used on the sample inlet to direct the sample through the NO_x converter, or directly to the valve oven. The valve oven contained two Valco multiport valves, and was temperature controlled. The first valve allowed injections of small sample volumes onto the column using constant volume (2.0 mL or 0.5 mL) Teflon loops. This method of introducing samples to the system was used to analyze samples of relatively higher (>15 ppbv) concentrations. Larger sample volumes passed through the cryogenic trap were measured by collecting the gas in an evacuated reservoir and monitoring the pressure change in the reservoir with a high precision pressure gauge. The second valve controlled gas flows

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Figure 3-5. Schematic Diagram of the NO_x Analytical System

through the GC column and cryogenic concentration loop. The GC column carrier gas was UHP grade Helium at a flow rate of 30 mL/min. The carrier gas flow was reversed (backflushed) when Valve 2 was switched. The cryogenic trap was cooled in liquid oxygen (-183°C) and heated with electrical heating cartridges. The NO_x analyzer was modified to allow manual selection of NO and NO_x modes, and a chromatographic integrator was used to process the signal from the NO_x analyzer. All equipment used (with manufacturer identified) is listed below:

- NO_x Analyzer: Columbia Scientific Industries Model CSI 600;
- Chromatographic Integrator: Hewlett Packard Model HP3390A;
- Temperature Controller: Omega Model 400 1KF;
- High Precision Gauge: Matheson No. 63-5601;
- Valve Oven and Cryogenic Traps: Designed and constructed by Radian Corporation.

Procedures

The analysis procedure involved warming up the NO_x analyzer for a minimum of one hour, conditioning the GC column, instrument calibration and sample analysis. All analyses were performed isothermally at room temperature. Normally, after the initial instrument warm-up period, the instrument remained on for all further on-site work. The column oven was heated to approximately 80°C overnight to remove collected impurities. The column was conditioned by several injections of a ppm-level standard. This was required to fill active sites on the column surface.

Analyses were performed by loop injection or cryotrap injection. Loop injections were performed by pulling standard or sample gases into the evacuated reservoir, closing the reservoir inlet valve, and switching the eight-port valve to its opposite position when the flow meter registered no-flow. The no-flow condition assured that all samples and standards were analyzed at the same pressure (atmospheric). Cryotrap injections were performed by pulling standard or sample gases through the cooled cryotrap and

into the evacuated reservoir. The pressure change of the evacuated reservoir was used to calculate the volume of air pulled through the cryotrap. After the appropriate volume was collected, the cryotrap was heated to 0°C and the cryotrap valve was switched to the inject position. The NO peak eluted in approximately one minute. After this peak eluted the cryotrap valve was switched to the backflush position to remove other components. For NO_x analyses, the same procedure was followed, but the initial three-way valve was switched to first route the sample through the NO_x converter.

Calibrations were performed using a 761 ppb NO gas standard obtained from Scott Environmental Technology (certification: ±2%). The standard was diluted to obtain lower concentrations using a dynamic flow calibration system. The efficiency of the NO_x converter was checked with an NO₂ permeation tube purchased from Kin-Tech Inc. High concentration standards (15-761 ppbv) were analyzed using loop injections and low concentration standards (5-50 ppbv) were analyzed by cryotrap injections. Calibrations were performed prior to sample analysis and intermittently between sample analyses. A response factor was calculated based on instrument response to the analyzed volume of standard using the same procedure discussed in the previous section. For the field sampling effort all calibration data for the first three days were combined to obtain an average response factor. A change in the instrument response was observed on the last day of the sampling effort, so a separate calibration was used for this day.

Method Validation

A considerable amount of method validation work was performed to assure specificity of the NO_x method, and to define the analytical detection limit, precision, accuracy, linearity, and storage stability. Results of the method validation work for NO_x species are summarized in this section.

Specificity. Several volatile organic species were tested for potential interferences in the NO_x method. Ethylene, COS, H₂S, CS₂, and several mercaptans showed no interferences with the column system which was used.

Linearity and Detection Limits. Since it was not possible to purchase ppb level standards of NO and NO₂, a ppm level standard of NO was purchased and diluted to the appropriate levels with a dynamic capillary dilution system. For NO₂, a calibrated permeation device was used. Because of limitations in the dilution system, it was not possible to dilute the NO standard to 1 ppb. The NO₂ standard from the permeation device could only be diluted to the 10 ppbv range. During the methods development and validation studies, 1 ppb levels of NO and NO₂ were simulated by analyzing small volumes of higher concentration standards. The analytical system was designed to use a wide range of analysis volumes.

A plot of system response as a function of the quantity of NO and NO₂ analyzed is presented in Figure 3-6. The absolute quantities of NO and NO₂ analyzed are listed on the left y-axis and the corresponding concentrations for a 175 mL sample volume are listed on the right y-axis. Three replicate analyses were performed at each concentration. Excellent linearity was obtained for both NO and NO₂. Correlation coefficients of 0.9999 were obtained for both NO and NO₂ calibrations. The lowest amount of NO analyzed was 0.18 nL, which corresponds to a concentration of 1 ppbv for an analysis volume of 175 mL. In the same manner, the lowest amount of NO₂ analyzed was 0.069 nL. Given the same 175 mL sample volume, this corresponds to a concentration of 0.4 ppbv. The excellent linearity at these levels demonstrates that a detection limit of 1 ppbv can be quoted for this method for simple matrix gases.

Similar linearity was obtained for calibration data obtained during the field sampling effort. These data are presented in the results section.

Replicability. Replicability of NO and NO₂ determinations on standard gases (in UHP N₂) is presented in Table 3-7. The actual concentration analyzed, volume analyzed, and the corresponding absolute quantities of NO and NO₂ are listed, along with the replicability at each concentration. Replicabilities were 5% or better at quantities above 0.5 nL (2.5 ppb for a

70A3185

Figure 3-6. Linearity of Nitric Oxide (NO) and Nitrogen Dioxide (NO₂)

Table 3-7
 REPLICABILITY OF NITRIC OXIDE AND NITROGEN DIOXIDE DETERMINATIONS

Parameter	Quantity Analyzed (nL) ¹	Concentration (ppb)	Volume Analyzed (mL)	Number of Analyses	Replicability (% CV) ²	Pooled CV (% CV) ²
Nitric Oxide	4.43	25.3	175	3	0.3	10.7
	1.72	9.8	175	3	5.0	
	0.89	5.1	175	3	5.0	
	0.18 ³	5.1	35	4	20.2	
Nitrogen Dioxide	2.43	1214	2.00	3	2.4	11.3
	0.607	1214	0.500	3	5.5	
	0.552	276	2.00	5	4.0	
	0.276	138	2.00	3	9.4	
	0.069 ³	138	0.500	3	22.2	

¹Nanoliters (10⁻⁹ L) of compound analyzed.

²Percent coefficient of variation.

³Corresponds to 1 ppbv or less for a 175 mL analysis volume.

175 mL analysis). Pooled CVs were approximately 10% for both species at all levels tested.

To determine method replicability for determining NO in actual samples, process gas from vent T1059 (collected 1/14/83) was analyzed in duplicate. The mean concentration measured was 38.9 ppbv with a percent coefficient of variation for this duplicate analysis of 1.8%. The average replicability for NO determinations for samples collected during the May field sampling effort was 28% for replicate analysis of five different samples.

Accuracy and Applicability. Analysis of process sample V104 overhead vent, with and without NO spike, is presented in Figure 3-7. NO was not observed in the unspiked sample. The large response which was observed at 1.5 minutes resulted from backflushing other stream parameters off the column. The spiked sample demonstrated that even with the large quantities of potentially interfering species present, NO can be differentiated with ease. The spiking studies showed recoveries greater than 80% for process gas samples.

Storage Stability. Since NO and NO_x are very reactive species, samples were analyzed onsite to reduce storage time. Tedlar® bags were used to collect samples for NO_x analyses since this material is more inert than stainless steel. Samples were always guarded from light since light catalyzes the reaction of NO_x with hydrocarbons. However, it was still necessary to determine storage stability for NO and NO₂ over several hours. Results of spiking a very low concentration of NO into Tedlar® bags are presented in Table 3-8. These data demonstrate no change over a three-hour period. They also demonstrate the consistency of the analytical method at these concentrations. Results from storage of an actual sample in Tedlar® bags for NO_x are presented in Table 3-9. These data demonstrated a CV of 6.5% over a four-hour period and maximum sample degradation of 10.5%.

Figure 3-7. Analysis of Sample V104 Overhead Vent With and Without Nitric Oxide Spike

Table 3-8

RESULTS OF STABILITY STUDY FOR NO IN TEDLAR® BAGS

<u>Elapsed Time¹</u> <u>(hr:min)</u>	<u>NO Concentration</u> <u>(ppbv)</u>
0:10	3.7
1:02	4.3
1:59	4.1
3:03	3.3

¹From the time that the bag was filled.

Table 3-9

RESULTS OF STABILITY STUDY FOR NO_x¹ IN
TEDLAR® SAMPLING BAGS

<u>Elapsed Time (hr:min)</u>	<u>NO_x Concentration (ppbv)</u>
0:10	4640
0:44	4810
1:41	4370
4:27	4150
Average:	4490
% CV:	6.5%
% Decrease:	10.5%

¹Bag filled with Sample T1059. Results show the analytical and sampling variation on an actual sample over time.

Application Results

The method developed for NO_x determinations was applied to samples collected during three time periods, as discussed previously. Results for all analyses are presented in Table 3-10. The results are arranged by stream to illustrate variations observed during different sampling periods. One stream with significant variability over time was the T1059 inlet. Since little is known by Radian concerning the effect of operating conditions on this stream, it is not possible to draw any conclusions on the significance of the observed variation for this stream. In general, the consistency of the results demonstrates proper functioning of the method. Further sampling of the T1059 inlet is recommended.

Quality Control. Quality control for the methods development activity was discussed under validation results. On-site quality control consisted of multiple instrument calibrations and replicate sample analyses. A total of 70 calibration runs at nine different concentrations were performed over the field sampling effort. Data for these calibrations are summarized in Tables 3-11 and 3-12. Calibration data for the first three days were combined since the instrument response was essentially constant. On the last day of field sampling, a change in the instrument response factor was observed. All data from that day were obtained using the latter response factor. Excellent linearity was obtained for both sets of calibration data. Correlation coefficients were 0.9998 and 0.9997 for the two calibrations. A plot of calibration data is presented in Figure 3-8. This figure demonstrates the excellent linearity obtained for quantities of NO down to levels less than 10 ppbv for a 46 mL sample size.

A summary of all NO data collected during the field sampling effort is presented in Table 3-13. Multiple analyses by loop injection were performed on four samples. Seven samples were analyzed by both loop and cryotrap. In all cases, results between the two techniques agreed, demonstrating no losses of NO occurred during the cryogenic trapping and thermal desorption. The overall analytical variation (pooled CV) was 28% for loop and cryotrap

Table 3-10

SUMMARY OF ANALYTICAL RESULTS FOR NO AND NO_x

Sample Stream	Collection Date	Analysis Date	NO Concentration (ppbv)	NO _x Concentration (ppbv)
V104	1/14/83	3/4/83	29	28
	2/16/83	2/24/83	<1	21
	5/8/83	5/8/83	<1	<15
	5/8/83	5/8/83	<1	<15
V105	1/14/83	3/9/83	2.9	140
V105/T104	5/7/83	5/7/83	64	51
	5/7/83	5/7/83	58	81
V106	1/14/83	3/9/83	24	45
	5/8/83	5/8/83	34	42
	5/8/83	5/8/83	14	18
T1059 Inlet	1/14/83	3/9/83	39	4600
	5/9/83	5/9/83	3.3	<12
	5/9/83	5/9/83	2.0	NA ¹
T1059 Outlet	5/9/83	5/9/83	3.4	NA ¹
	5/9/83	5/9/83	10.3	NA ¹

¹NA = Not analyzed - contamination of NO₂ catalyst converter.

Table 3-11

SUMMARY OF FIELD CALIBRATION RESULTS FOR NO
(May 6-8, 1983)

<u>nL-C</u>	<u># Points</u>	<u>Ave. Response (area/nL-C)</u>	<u>Ave. Area ÷ 1000</u>	<u>% CV</u>	<u>Comments</u>
3.805	12	2172	8263	9.0	5/8, 5/9/83
1.522	19	2215	3373	8.7	5/6-5/8
0.3044	6	1839	575	13.0	5/7
0.2725	2	1898	517	11.7	5/8
0.125	4	597	74.6	9.4	5/8
0.109	3	650	70.9	14.6	5/8

Slope = 2212

Y-int. = -120

C.C. = 0.9997

X-int. = 0.0543

Table 3-12

SUMMARY OF FIELD CALIBRATION RESULTS FOR NO
(May 9, 1983)

<u>nL-C</u>	<u># Points</u>	<u>Ave. Response (area/nL-C)</u>	<u>Ave. Area ÷ 1000</u>	<u>% CV</u>	<u>Comments</u>
3.805	5	1593	6061	8.8	5/9/83
1.522	5	1629	2479	20.4	5/9/83
0.1660	2	1634	271	16.1	5/9/83
0.0972	3	710	69.0	9.2	5/9/83
0.0664	3	298	19.8		5/9/83

Slope = 1611

Y-int. = -43

C.C. = 0.09998

X-int. = 0.0269

Figure 3-8. NO_x Calibration Results for Field Sampling

Table 3-13

STATISTICAL ANALYSIS OF NO FIELD DATA¹

Sample #	Sample Stream	NO by Loop (ppbv)	NO by Cryotrap (ppbv) ²	Average Sample NO Mean + SD (CV) n ³	Average Stream NO Mean ± SD (cv) ⁴
1	V105/T104	72.6	55.8	64.2±11.9 (18.5) 2	61.1± 4.5 (7.3)
2	V105/T104	57.9		57.9±18.8 (32.5) 3	
3	V106	34.3		34.3±11.6 (33.8) 3	24.2±14.4 (59.4)
4	V106	14.0		14.0± 1.8 (12.9) 4	
5	V104	<14	<1	<1	<1±<1
6	V104	<14	<1	<1	
7	T1059 Inlet	<14	3.3	3.3	2.7± 0.9 (34.7)
8	T1059 Inlet	<14	2.0	2.0	
9	T1059 Outlet	<14	3.4	3.4	7.5± 5.7 (76.9)
10	T1059 Outlet	<14	11.5	11.5	
Pooled Averages				12.6 (28.1)	8.1 (51.7)

¹All results in ppbv NO.²Only single analyses performed.³Total number of sample analyses (loop + cryotrap).⁴Average for both samples from each stream.

analyses combined. The pooled analytical standard deviation was 13 ppbv. The data variation between duplicate samples, taking into account temporal (source) and sampling effects, was 52%. This figure is somewhat misleading since it is influenced heavily by large relative variations of low concentration samples. The pooled standard deviation between samples was 8 ppbv.

Section 4

DESCRIPTION OF SAMPLING AND ANALYSIS METHODOLOGY

Sampling was conducted over three days of process operation (May 7-9, 1983) at the advanced two-stage coal liquefaction research unit in Wilsonville, Alabama. The following sections present the information and methodology for the sampling effort and chemical analyses.

SAMPLING

Gas phase samples were collected by Radian from five points in the process. Plant personnel collected samples of the raw coal and process solvent. The sampling schedule, definition of the sample points, and procedures used in the sample acquisition are presented as a reference.

Sampling Schedule

Figures 4-1, 4-2 and 4-3 present the sampling activity schedule for the three individual days. On Day 1 (May 7, 1983) Radian sampled Stream #3, a combined stream consisting of the high pressure V105 overhead vent from the Solvent Decanter and low pressure T104 vent from the fractionating column. Two samples each of cyanide impingers, ammonia impingers, mercury tubes and gas bombs/gas bags were collected for analysis. A continuous 10-hour impinger sampling was performed for trace element determination and a continuous 4-hour impinger sample was collected for halide determination.

Similar samples were collected on Day 2 and Day 3. On Day 2 (May 8, 1983) samples were collected from Stream #1 (the high pressure vent on the overhead of the V104 separator) and Stream #2 (the high pressure overhead gas of the V106 water scrubber).

Figure 4-1. Day 1 Sample Collection Schedule

Figure 4-2. Day 2 Sample Collection Schedule

Figure 4-3. Day 3 Sample Collection Schedule

The two streams of Day 3 (May 9, 1983) included Stream #6 (the hydrotreater recycle gas entering the T1059 scrubber) and Stream #7 (the hydrotreater vent gas exiting the T1059 scrubber).

Catalytic personnel collected raw coal and process solvent samples as defined below:

<u>Raw Coal from Lockhopper Feed to V101A & B</u>		<u>Process Solvent from V131B</u>	
5/7/83	1700 hours	5/7/83	1700 hours
5/7/83	1930 hours	5/8/83	1930 hours
5/9/83	dayshift (exact time not specified)	5/9/83	dayshift (exact time not specified)
5/9/83	1820 hours	5/9/83	1835 hours

Sample Points

Figure 4-4 presents a simplified flowsheet of the first stage (SRC) of the liquefaction process and the location of streams sampled. A flowsheet of the second stage (hydrotreater unit) and gas streams sampled is presented in Figure 4-5. Gas streams sampled include:

- Stream #1 - high pressure overhead gas of the V104 separator of the first stage. This stream was raw recycle gas composed primarily of hydrogen. It was cooled in the process to allow removal of condensables.
- Stream #2 - high pressure overhead gas of the V106 water scrubber of the first stage. This gas is similar in composition to that of Stream #1 but has been also subjected to caustic and water scrubbing for trace contaminants removal.
- Combined Streams #3 and #4 - combination of solvent decanter vent gas from V105 and fractionating column flare gas from T104.

Figure 4-4. SRC Flowsheet

Figure 4-5. Hydrotreater Flowsheet

- Stream #6 - Vent gas from several process points of the hydrotreater unit including flash vessels, reflux tank and excess recycle gas. This stream was sampled where it entered the T1059 scrubber.
- Stream #7 - hydrotreater vent gas exiting the T1059 scrubber. The scrubber operated with water as opposed to caustic during the sampling period.

Also sampled were the raw coal and process solvent. Plant personnel collected the raw coal from the feed lockhoppers prior to attachment to the V101A & B slurry blend tanks. Process solvent was collected by plant personnel from V131.

Sampling Procedures

Plant personnel constructed three portable, stainless steel gas manifold systems to allow sample collection at different process points. Radian used a consistent gas sampling methodology at each point.

Gas Manifold System. The gas manifold system displayed in Figure 4-6 consisted of a needle valve to isolate and coarsely adjust gas volume, a knockout pot to retain condensables, a pressure relief valve, and three sample taps for gas collection. Each sample tap included a flowmeter with adjustment valve for fine control of gas flow. Two flowmeters were selected for the system:

- One with a range of 0-20 SCF hr, and
- One with a range of 0-130 SCC min.

Three types of samples were collected from the system:

- Impinger sorption solutions for collection of soluble components,
- Tubes containing gold mesh plugs for amalgamation of mercury, and
- Gas bombs for on-site and off-site gas analyses.

Figure 4-6. Schematic of the Gas Sampling Manifold System

Figure 4-7 presents the complete gas sampling system.

Impinger Collection. The gas was directed through a series of impingers contained in an ice bath for sorption of the component of interest. Gas was sampled up to a maximum flowrate of 0.4 ACFM (meter conditions). Stream pressure was used as the driving force for gas sampling.

Ammonia. Ammonia was collected from the gas stream with two impingers in series each containing approximately 200 mL of 5 percent H_2SO_4 . These two impingers were followed by a dry impinger and an impinger containing indicating silica gel desiccant. The impingers were cooled with ice water.

Hydrogen cyanide. Collection of hydrogen cyanide was accomplished using two impingers in series each containing approximately 200 mL of 10 percent sodium hydroxide. These were followed by two impingers, one dry and one containing silica gel desiccant. The impingers were cooled with ice water.

Halides (chloride and fluoride). Halides were collected from the gas stream with two impingers in series each containing approximately 200 mL of 1 percent NaOH . These two impingers were followed by a dry impinger and an impinger containing silica gel desiccant. The impingers were cooled with ice water.

Volatile trace elements. Volatile trace elements were collected in an ice cooled impinger train using both acidic and basic solutions. The impinger train consisted of the following series of impingers:

- Two Smith-Greenburg impingers containing approximately 200 mL of 10 percent nitric acid,
- One dry modified Smith-Greenburg impinger,
- Two Smith-Greenburg impingers containing approximately 200 mL of 5 percent sodium hydroxide,

Figure 4-7. Complete Gas Sampling System

- One dry modified Smith-Greenburg impinger, and
- One modified Smith-Greenburg impinger containing indicating silica gel desiccant.

Vaporous Mercury. Vaporous mercury was collected by passing a volume of gas through a quartz tube containing a gold wire plug. A flowrate of 300 to 400 mL per minute was passed through the tube for various lengths of time ranging from 5 minutes to 3 hours. Flowrates of the gas were measured using a calibrated rotameter.

Gas Chromatography Samples. Gas samples for analysis by gas chromatography were taken at each sampling location. Samples were collected in 2-liter Tedlar® bags which were encased in a second container to minimize exposure to sunlight. Depending on the process pressure, samples were collected over a one- to ten-minute period.

At the same time an additional gas sample was collected in an evacuated stainless steel canister for the off-site analysis of butadiene.

ANALYSIS METHODOLOGY

Onsite Analysis

A majority of the analyses were performed onsite. Table 4-1 presents the methodology used in the characterization.

Fixed Gases. Fixed gases (CO_2 , H_2 , O_2 , N_2 , CH_4 , CO , and H_2S) were determined by gas chromatography with a thermal conductivity detector under the following analytical conditions:

Instrument: Fisher Model 1200 Gas Partitioner

Analytical Columns:

1. 2 m x 3.2 mm OD stainless steel packed with 80/100 mesh Porapak Q
2. 6.7 m x 4.8 mm OD aluminum packed with 25% KOH or 80/100 mesh Chromasorb P-AW
3. 3.4 m x 4.8 mm OD aluminum packed with 80/100 mesh Molecular Sieve 13X.

Table 4-1
ANALYSIS METHODS FOR IMPINGER SOLUTIONS

<u>Analyte</u>	<u>Method</u>	<u>Reference</u>
NH ₃	Potentiometry	EPA Method 350.2
CN ⁻	Distillation/Colorimetry	EPA Method 335.2
SCN ⁻	Colorimetry	SM 412K
F ⁻	Specific Ion Electrode	EPA Method 340.2
Cl ⁻	Potentiometric Titration	SM 407C
Be	Atomic Absorption Spectrophotometry with Graphite Furnace	EPA Method 210.2
As	Atomic Absorption Spectrophotometry with Graphite Furnace	EPA Method 206.2
Pb	Atomic Absorption Spectrophotometry with Graphite Furnace	EPA Method 239.2

Carrier: 30 mL/min, 8.5% H₂ in He (zero grade)

Column Temperature: 70°C

Bridge Current: 275 mA

Certified standards (Ideal Gas Products, Edison, NJ, and Scientific Gas Products, S. Plainfield, NJ) and dilutions of these standards were analyzed to establish calibration curves and retention times.

Hydrocarbons (C₂-C₆). Gas-phase hydrocarbons were analyzed using a gas chromatograph equipped with flame ionization detector under the following analytical conditions.

Instrument: Antek Model 460 GC-FID

Analytical Column: 10 ft x 1/8" stainless steel packed with 80/100 mesh preconditioned Porapak Q

Carrier: N₂ (zero grade) 30 mL/min

Oven Program: 50°C for 5 min; 10°C/min to 250°C

A certified gas standard obtained from Scott Specialty Gases, Plumsteadville, PA, and dilutions were analyzed to determine detector response for methane and propane on a % · C basis. Retention times for C₂-C₆ species were determined by analyzing certified gas standards for C₁-C₆ paraffins and C₂-C₆ olefins.

Sulfur Species. Sulfur species (COS, CS₂, SO₂, mercaptans and thiophene) were determined by gas chromatography using a flame photometric detector. An Antek Model 460 GC-FPD was used to perform the analysis according to EPA Method 15.

NO_x. NO_x was determined by the developed method described in Section 3.

Off-Site Analyses

Additional analyses performed offsite included characterization of impinger solutions, trace element analysis of the raw coal and process solvent, and butadiene analysis of process gases.

Impinger Solution Analyses. Impinger solutions were analyzed by either EPA or Standard Methods as listed in Table 4-1. Samples were preserved onsite prior to shipment for those components susceptible to degradation.

Trace Element Analysis of Raw Coal and Process Solvent. Samples of the raw coal and process solvent required digestion prior to analysis. Preparation steps are presented in Figure 4-8. References for preparation activities are listed in Section 5.

Butadiene Analysis. Butadiene was determined by the developed method described in Section 3.

Hg EPA METHOD 246.1

Be EPA METHOD 210.2

F EPA METHOD 340.2

As EPA METHOD 206.2

Pb EPA METHOD 239.2

LTA-LOW TEMPERATURE ASHING (REF. 1)

70A3364

PAD-PERCHLORIC ACID DIGESTION (REF. 2)

Na₂CO₃ FUSION (REF. 3)

HNO₃/H₂O₂ DIGESTION (REF. 4)

Figure 4-8. Preparation and Metals Analysis

Section 5

REFERENCES

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APPENDIX A
COMPARISON OF ON-SITE AND OFF-SITE GAS ANALYSES

COMPARISON OF ON-SITE AND OFF-SITE GAS ANALYSES

Component, Concentration Units	1 H.P. Vent Separator (V104 Overhead)		2 Water Scrubber (V106 Overhead)		3/4 Solvent Decanter/ Column Vents (V105/V104)		6 Hydrotreater Recycle (T1059 Inlet)		7 Hydrotreater Vent (T1059 Outlet)	
	On-Site	Off-Site	On-Site	Off-Site	On-Site	Off-Site	On-Site	Off-Site	On-Site	Off-Site
H ₂ , %	82.2	81.3	83.8	83.0	35.2	30.6	86.9	85.8	87.4	86.4
CO, %	0.90	1.19	0.85	1.08	0.21	0.16	ND(0.01)	ND(0.01)	ND(0.01)	ND(0.01)
CO ₂ , %	0.38	0.30	0.02	0.01	0.46	0.46	ND(0.01)	ND(0.01)	ND(0.01)	ND(0.01)
N ₂ , %	0.71	0.55	0.38	0.40	34.9	37.6	9.6	10.8	9.9	11.0
C ₁ , %	9.8	10.4	9.7	10.2	7.6	8.4	1.18	1.21	0.89	0.88
C ₂ (Ethylene), %	0.03	0.02	0.03	0.03	0.03	0.04	ND(0.01)	ND(0.01)	ND(0.01)	ND
C ₂ (Ethane), %	3.3	3.4	3.2	3.2	6.3	6.6	0.70	0.68	0.55	0.54
C ₃ , %	1.5	1.6	1.5	1.5	6.2	6.4	0.39	0.40	0.31	0.30
C ₄ , %	0.41	0.44	0.39	0.42	3.5	3.8	0.13	0.13	0.11	0.10
C ₅ , %	0.09	0.10	0.08	0.08	1.3	1.6	0.05	0.04	0.04	0.04
C ₆ , %	0.06	0.02	0.08	0.07	0.87	0.90	0.16	0.11	0.20	0.14

¹Determined by difference.