



Polymers and Resins

Volatile Organic Compound Emissions from Incineration

Emission Test Report ARCO Chemical Company LaPorte Plant Deer Park, Texas

Volume I: Summary of Results



DCN #82-222-018-07-06

POLYMERS AND RESINS

VOLATILE ORGANIC COMPOUND
EMISSIONS FROM INCINERATION

EMISSION TEST REPORT
ARCO CHEMICAL COMPANY
LAPORTE PLANT
DEER PARK, TEXAS

VOLUME 1: SUMMARY OF RESULTS

FINAL REPORT

EPA Contract No. 68-02-3542
Work Assignment 07
ESED 78/24

Prepared for:

Winton Kelly
U.S. Environmental Protection Agency
ESED/EMB (MD-13)
Research Triangle Park, North Carolina 27711

Prepared by:

K.W. Lee, C.J. Thielen,
D.L. Lewis, J.L. Randall, J.R. Boettcher and
Program Manager - J.W. Kamas
Radian Corporation
8501 Mo-Pac Boulevard
Austin, Texas 78759

31 March 1982

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
LIST OF TABLES	vi
LIST OF FIGURES	ix
ACKNOWLEDGMENT	x
GLOSSARY OF ACRONYMS	xi
1.0 INTRODUCTION	1
2.0 SUMMARY OF RESULTS	4
2.1 Destruction Efficiencies	4
2.2 Process and Gas Phase Data.	8
2.3 Composition of Atactic Waste and NO _x Levels	12
3.0 PROCESS AND INCINERATOR DESCRIPTIONS	16
3.1 Process Description	16
3.2 Incinerator Description	17
4.0 SAMPLING METHODOLOGY	23
4.1 Description of Sampling Points	23
4.1.1 Incinerator Inlet.	23
4.1.2 Waste Heat Boiler Outlet	25
4.1.3 Scrubber Stack Outlet.	25
4.2 Volatile Organic Carbon Sampling Methods.	25
4.2.1 EPA Method 25	25
4.2.2 Proposed EPA Method 18	26
4.2.3 Byron Method	30
4.3 NO _x Sampling at Waste Heat Boiler Stack	31

TABLE OF CONTENTS (Continued)

<u>Section</u>	<u>Page</u>
4.4 Scrubber Stack Volumetric Flow Rate	33
4.5 Flue Gas Molecular Weight and Flue Gas Moisture	33
4.6 Atactic Waste Sampling.	35
4.7 Waste Gas Stream.	37
4.8 Natural Gas	37
4.9 Miscellaneous Readings	37
5.0 ANALYTICAL METHODOLOGY	39
5.1 Gas Analysis	39
5.1.1 Proposed Method 18 for Hydrocarbons	39
5.1.2 Byron Total Hydrocarbon Analyzer	41
5.1.3 Volatile Organic Compounds (VOC's) - EPA Method 25 .	42
5.1.4 Hydrocarbon Speciation	42
5.1.5 Fixed Gases	43
5.1.6 NOx	44
5.1.7 BGI Filters	44
5.2 Aqueous Condensate Analysis	45
5.2.1 Total Organic Carbon (TOC)	45
5.2.2 Inorganic Species	46
5.3 Atactic Waste Analysis	47
5.3.1 Ultimate, Proximate, Btu Content	47
5.3.2 Moisture	47

TABLE OF CONTENTS (Continued)

<u>Section</u>	<u>Page</u>
6.0 QUALITY ASSURANCE	48
6.1 Summary of Audit Results and Conclusions	48
6.2 Systems Audit - Approach and Conclusions	51
6.3 Performance Audit.	53
6.3.1 Methods for Quantitation of Accuracy and Precision. .	54
6.3.2 Quantitation of Data Quality.	60
7.0 RESULTS	82
7.1 Gas Phase Data	82
7.1.1 Volatile Organic Carbon (VOC) Measurement	87
7.1.2 Hydrocarbon Speciation Results	90
7.1.3 Fixed Gases	93
7.1.4 BGI Filters	93
7.2 Total Organic Carbon (TOC) Analyses of Aqueous Condensate .	95
7.3 Atactic Waste Analysis	95
7.4 Calculations	95
7.4.1 Calculation of Destruction Efficiencies	95
7.4.2 Calculation of Excess Oxygen.	103
7.5 Miscellaneous Analyses	103
7.5.1 Inorganic Species	104
7.5.2 NOx	104

TABLE OF CONTENTS (Continued)

<u>Section</u>	<u>Page</u>
REFERENCES	113
APPENDIX A	
APPENDIX B	
APPENDIX C	
APPENDIX D	
APPENDIX E	
APPENDIX F	
APPENDIX G	

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1-1 TEST MATRIX FOR INCINERATOR VARIABLES.	2
2-1 INCINERATOR DESTRUCTION EFFICIENCIES FOR EACH SET OF CONDITIONS. .	5
2-2 INCINERATOR DESTRUCTION EFFICIENCIES (CALCULATIONS BASED ON WASTE GAS ONLY).	7
2-3 INCINERATOR DESTRUCTION EFFICIENCIES (METHOD 18 ANALYSIS OF GASEOUS HYDROCARBONS AND IMPINGER TOC)	9
2-4 INCINERATOR DATA SUMMARY - AVERAGE VALUES FOR EACH SET OF INCINERATOR CONDITIONS.	10
2-5 PERCENT CARBON, Btu/LB AND PERCENT MOISTURE IN ATACTIC WASTE . . .	14
2-6 NO _x RESULTS FOR SELECTED INCINERATOR CONDITIONS.	15
3-1 TYPICAL INCINERATOR PARAMETERS BASED ON DATA FROM AUGUST, 1981 (PROVIDED BY ARCO CHEMICAL COMPANY FROM PROCESS DATA).	21
5-1 METHODS USED TO DETERMINE THE INORGANIC SPECIES.	46
6-1 SUMMARY OF ESTIMATED VERSUS MEASURED DATA QUALITY.	50
6-2 AUDIT STANDARDS.	54
6-3 SUMMARY OF PRECISION OF HYDROCARBON DETERMINATIONS	61
6-4 SUMMARY OF PERFORMANCE AUDIT RESULTS FOR METHOD 18 ON-SITE HYDROCARBON DETERMINATIONS	63
6-5 PERFORMANCE AUDIT RESULTS FOR OFF-SITE METHOD 18 HYDROCARBON SPECIATION	65
6-6 SUMMARY OF PRECISION FOR OFF-SITE METHOD 18 HYDROCARBON SPECIATION	66
6-7 SUMMARY OF EPA METHOD 25 PERFORMANCE AUDIT RESULTS	67
6-8 SUMMARY OF PERFORMANCE AUDIT RESULTS FOR BYRON METHOD ANALYSES . .	68
6-9 SUMMARY OF PRECISION OF TOC ANALYSES	70

LIST OF TABLES (Continued)

<u>Table</u>		<u>Page</u>
6-10	SUMMARY OF PERFORMANCE AUDIT DATA FOR TOC ANALYSES.	71
6-11	SUMMARY OF ANALYTICAL PRECISION OF PROXIMATE AND ULTIMATE ANALYSES	72
6-12	SUMMARY OF PERFORMANCE AUDIT RESULTS FOR PROXIMATE AND ULTIMATE ANALYSES	73
6-13	SUMMARY OF ANALYTICAL REPLICABILITY OF WATER DETERMINATION. . . .	74
6-14	SUMMARY OF PERFORMANCE AUDIT RESULTS FOR KARL-FISCHER MOISTURE DETERMINATIONS	75
6-15	SUMMARY OF PERFORMANCE AUDIT RESULTS FOR FIXED GAS ANALYSES . . .	77
6-16	SUMMARY OF PRECISION FOR FIXED GAS DETERMINATIONS	78
6-17	SUMMARY OF PRECISION FOR NO _x ANALYSES	80
6-18	SUMMARY OF NO _x AUDIT SAMPLE ANALYSES.	81
7-1	INCINERATOR DATA SUMMARY FOR EACH SAMPLING RUN.	83
7-2	INCINERATOR DATA SUMMARY - AVERAGE VALUES FOR EACH SET OF INCINERATOR CONDITIONS	88
7-3	HYDROCARBON SPECIATION OF BOILER OUTLET SAMPLES	91
7-4	PERCENT EXCESS OXYGEN FOR EACH SET OF OPERATING CONDITIONS. . . .	94
7-5	RESULTS OF ORGANIC ANALYSIS OF BGI FILTERS.	94
7-6	TOC LEVELS IN IMPINGER CATCHES.	96
7-7	IMPINGER CATCHES TOC VS. TOTAL SAMPLE TOC	97
7-8	PERCENT CARBON, Btu/LB AND PERCENT MOISTURE IN ATACTIC WASTE FOR EACH SET OF OPERATING CONDITIONS.	98
7-9	AVERAGE Btu/LB, PERCENT CARBON AND PERCENT MOISTURE IN ATACTIC WASTE FOR EACH DAY OF SAMPLING.	99

LIST OF TABLES (Continued)

<u>Table</u>		<u>Page</u>
7-10	RESULTS OF PROXIMATE, ULTIMATE, Btu CONTENT AND MOISTURE ANALYSES FOR ATACTIC WASTE.	100
7-11	PROCESS FLOW RATES DURING EACH SET OF OPERATING CONDITIONS. . . .	110
7-12	ARCO INCINERATOR IMPINGER CATCHES - INORGANIC ANALYSIS OF BOILER OUTLET SAMPLE.	111
7-13	NO _x RESULTS FOR SELECTED INCINERATOR CONDITIONS	112

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
3-1 Schematic of Incinerator Showing Inlet and Outlet Streams.	18
3-2 Incinerator System with Dimensions	20
4-1 Incinerator System with Sampling Point Locations.	24
4-2 Method 25 Sample Acquisition Apparatus	27
4-3 EPA Proposed Method 18 Sampling Apparatus.	28
4-4 Schematic Diagram of Byron Sample Acquisition Apparatus.	32
4-5 EPA Method 7 - NO _x Sampling Train.	34
4-6 Atactic Waste Sampling Bomb.	36

ACKNOWLEDGMENT

The authors wish to express their appreciation to the many individuals who contributed to this project. Special expression of gratitude for their beneficial contributions to the work described in this report go to:

Winton Kelly (United States Environmental Protection Agency - ESED/EMB - Research Triangle Park, North Carolina)

J.W. Parker, A.H. Bitzer and J. Requena (ARCO Chemical Company, LaPorte Plant, Deer Park, Texas)

H. Shukla and A. Limpiti (EEA, Research Triangle Park, North Carolina)

W. Draisker, F. Meadows and D.T. Robinson (Pollution Control Science, Inc., Miamisburg, Ohio)

C.N. Dominick, D.S. Lewis, R.D. Cox, S. Dennis and C.B. Chapman (Radian Corporation, Austin, Texas).

GLOSSARY OF ACRONYMS

ACFM	- Actual Cubic Feet Per Minute
AW	- Atactic Waste
BO	- Boiler Outlet
ΔP	- Pressure differential across pitot, used to measure gas velocity
EPA	- Environmental Protection Agency
FID	- Flame Ionization Dectector
GC	- Gas Chromatograph(y)
GRAV	- Gravimetric Residue After Evaporation
HC	- Hydrocarbons
NG	- Natural Gas
NMHC	- Nonmethane Hydrocarbons
NOx	- Oxides of Nitrogen
SCFM	- Standard Cubic Feet Per Minute
SO	- Scrubber Outlet
TCO	- Total Chromatographable Organics
THC	- Total Hydrocarbons
TNMHC	- Total Nonmethane Hydrocarbons
VOC	- Volatile Organic Carbon
WG	- Waste Gas

1.0 INTRODUCTION

This report presents the results of measurements of VOC (Volatile Organic Carbon) destruction efficiencies in ARCO Chemical Company's Monument II Plant incinerator (Deer Park, Texas) as a function of:

- 1) operating temperature, and
- 2) feed stocks, including waste gas and atactic (unsymmetrical) polymeric waste.

The measurements were performed by Radian Corporation from October 21 through October 29, 1981. This work was funded and administered by the Emission Measurement Branch of the U.S. Environmental Protection Agency. The purpose of these tests was to develop data to be used in support of New Source Performance Standards (NSPS) for the Polymers and Resins industry. The ARCO facility provided data on a relatively new and efficient incinerator. A secondary purpose of this project was to compare results of different analytical methods applicable to the measurement of VOC emissions.

The test matrix in the order performed is shown in Table 1-1. Eight conditions were tested. No high temperature test was performed for waste gas and natural gas because the incinerator could not maintain 2000°F using this gas mixture as fuel. The methods used to measure VOC emissions included:

- EPA Method 25,
- Proposed EPA Method 18 (both on-site and off-site analyses performed), and
- Byron Instruments Model 90 sample collection system and Model 401 Hydrocarbon Analyzer sampling system and instrument combination.

TABLE 1-1. TEST MATRIX FOR INCINERATOR VARIABLES

<u>FUEL MIXTURES</u>	<u>TEMPERATURE</u>		
	<u>1600°F</u>	<u>1800°F</u>	<u>2000°F</u>
Natural Gas + Waste Gas + Atactic Waste	4*	5	6
Natural Gas + Waste Gas	8	7	**
Natural Gas + Atactic Waste	2	1	3

* Listed in order performed.

** Incinerator could not maintain 2000°F using this fuel mixture.

The following sections present a summary of results, process and incinerator description, sampling and analytical methodologies, quality assurance/quality control and detailed results of all analyses. The appendices include a full listing of analytical and process data along with a complete evaluation of the Byron method for measuring VOC emissions.

2.0 SUMMARY OF RESULTS

This section summarizes the results given in detail in Section 7. The ultimate goal of this project was to determine the destruction efficiencies in the incinerator.

The volatile organic carbon (VOC) measurements were made by three independent methods under specified incinerator temperatures and fuel mixes. These measurements are compared in this section for the eight different conditions achieved by the incinerator.

2.1 Destruction Efficiencies

Destruction efficiencies (DE's) are based on calculated or measured values of the carbon contents of the waste stream inlets and the volatile organic carbon (VOC) content of the incinerator flue gas. The equation used to compute the percent destruction efficiencies of the waste streams is as follows:

$$\% \text{ Destruction Efficiency} = 100 - \left[\frac{\text{grams of VOC in Stack Gas}}{\text{grams Organic Carbon in Atactic Waste} + \text{grams of Organic Carbon in Waste Gas}} \times 100 \right]$$

where grams of VOC in the stack gas were measured by the four analytical methods and the amounts of carbon have been normalized by a set time interval (e.g., g/sec.). This computation does not represent overall combustion efficiency of the unit since the supplemental fuel (natural gas) is not included in the denominator

Table 2-1 contains the measured destruction efficiencies (DE's) based on analytical method and incinerator conditions. The values which have greater than signs (>) indicate that no volatile organic carbon (VOC) was measured and the detection level was used to calculate the DE's. Each

TABLE 2-1. INCINERATOR DESTRUCTION EFFICIENCIES
FOR EACH SET OF CONDITIONS

Conditions	% Destruction Efficiency†				
	Calculated for Each Method				
	GC HC	Byron THC	Byron NMHC	Method** 25	Speciated Hydrocarbons
AW/NG/WG @ 2,000°F	>99.99777±.00008	99.994±.002	99.997±.002	99.844±.006	
AW/NG/WG @ 1,800°F	>99.9979±.0004	99.996±.001	99.998±.001	99.8±.4	
AW/NG/WG @ 1,600°F	>99.99721±.00009	99.9961±.0003	99.9957±.0002	99.6±.2	
NG/WG @ 1,800°F	99.8±.1	99.9±.1	99.6±.4	76±20	
NG/WG @ 1,600°F	>99.76±.07	99.8±.10	99.88±.04	66±10	99.88±.04
AW/NG @ 2,000°F	99.99674±.00007	99.9941±.0001	99.99796±.00005	96.32±.08	
AW/NG @ 1,800°F	>99.990±.004	99.983±.007	99.983±.007	98±3	
AW/NG @ 1,600°F	>99.9975±.0001	99.994±.002	99.995±.003 *	99±1	99.9979±.0001

* Difficulties with analysis - Based on most probable value

** Data not believed to represent true values.

† % Destruction Efficiency - $100 - \left[\frac{\text{grams of organic carbon (gC) in Stack Gas}}{\text{grams of carbon (gC) in Atactic Waste} + \text{grams of carbon (gC) in Waste Gas}} \times 100 \right]$

sampling and analytical method combine to define VOC levels in the incinerator outlet. However, careful inspection of the DE's indicate that nearly all VOC numbers under each condition overlap when measured by the proposed EPA Method 18, the Byron 401 in the total hydrocarbon (THC) mode, the Byron 401 in the non-methane hydrocarbon (NMHC) mode and the off-site, detailed hydrocarbon speciation method. The absolute values for the DE's by EPA Method 25 are consistently lower and of poorer quality. The poorer quality is indicated by the overall larger standard deviations; this is further discussed in the Quality Assurance/Quality Control Section (Section 6.0). The VOC values by EPA Method 25 and any data resulting from their use are questioned as to representing true values. The Byron 401 NMHC mode had a similar problem but this was rectified on-site (see Appendix D for details).

When the waste gas was the only waste to the incinerator, the DE's appear to be lower. The waste gas carbon flow rate (~ 1.8 g/sec, see Table 7-10) was very low compared to the natural gas (~ 110 g/sec) which was used as a supplemental fuel with the waste gas. VOC measured under these conditions was compared to a very small number (waste gas carbon flow rate) to obtain the DE. If any VOC was measured, the DE for the waste gas appeared to be somewhat lower than other waste stream combinations while it may instead be due to the natural gas contribution to the VOC. Natural gas alone was not one of the conditions tested.

There is interest in the waste gas DE's when waste gas was used as a minor fuel component with atactic waste as the major component. When this test condition existed, natural gas was also used as a minor fuel component. The DE's calculated for the waste gas only using this three-component fuel mixture are given in Table 2-2. Again, because of low carbon contributions from the waste gas ($\sim 1\%$ of the total fuel mixture) very low VOC values still could result in somewhat lower waste gas DE's. If Method 25 results are ignored, the DE's based on the waste gas only are still above 99.5%.

TABLE 2-2. INCINERATOR DESTRUCTION EFFICIENCIES*
(CALCULATIONS BASED ON WASTE GAS ONLY)

	% DESTRUCTION EFFICIENCY			
	GCHC	BYRON THC	BYRON NMHC	METHOD** 25
AW/NG/WG 1600°F	>99.81±.12	99.74±.17	99.71±.18	73±20
AW/NG/WG 1800°F	>99.750±.009	99.58±.15	99.73±.13	22±50
AW/NG/WG 2000°F	>99.83±.02	99.54±.13	99.79±.13	89±1

* % Destruction efficiency = $100 - \left[\frac{\text{gC in stack gas as VOC}}{\text{gC in waste gas}} \times 100 \right]$

** Not believed to be true values.

Moisture was a problem during sampling of the incinerator outlet gases (at the Waste Heat Boiler); therefore, a series of two small, dry impingers were used to condense the moisture before entering any of the three sampling systems. Only a few drops of aqueous condensate were collected during each run. This amount was rinsed out with distilled water (25 ml) and sent back to Radian's Austin laboratory for total organic carbon (TOC) analysis. Even though the blank for the distilled water was relatively high (~3 ppm), some samples were above this blank. If this organic material is defined as VOC then it must be added to the VOC measured by the methods for gas phase VOC. The results of these additions are listed in Table 2-3. In one set of incinerator conditions, this addition increased the amount of VOC as much as fifty times the level seen in the gas phase. However, the relative error in the TOC measurements is large in most instances and the percent DE values for gaseous hydrocarbons alone and gaseous hydrocarbons with the impinger catches overlap within the calculated standard deviations.

2.2 Process and Gas Phase Data

Table 2-4 summarizes the important process and gas phase data for each of the eight incinerator conditions. The table includes results of gas analyses on samples taken from the Boiler Outlet (BO), waste gas (WG) and natural gas (NG) sampling points.

The first, readily apparent, observation is that the proposed EPA Method 18 (on-site and off-site) results and the two types of measurements made by the Byron Method are similar in values. The averages and standard deviations overlap in most cases. The EPA Method 25 values for VOC from the Boiler Outlet are 100 to 1000 times greater than the other methods. This difference suggests that the Method 25 data may not represent true values and that the method may have an inherent problem when applied to combustion processes.

TABLE 2-3. INCINERATOR DESTRUCTION EFFICIENCIES
(METHOD 18 ANALYSIS OF GASEOUS
HYDROCARBONS AND IMPINGER TOC)

CONDITIONS	% D.E. GASEOUS HYDROCARBONS	% D.E. IMPINGER TOC	% D.E. GASEOUS HC AND IMPINGER TOC
AW/NG/WG @ 2000°F	>99.99777±.00008	99.90±.02	>99.90±.02
AW/NG/WG @ 1800°F	>99.9979±.0004	99.995±.005	>99.993±.005
AW/NG/WG @ 1600°F	>99.99721±.00009	NA	>99.99721±.00009
NG/WG @ 1800°F	99.8±.1	99.4±.6	99.2±.7
NG/WG @ 1600°F	>99.76±.07	99.3±.7	>99.1±.7
AW/NG @ 2000°F	99.99674±.00007	99.991±.008	99.988±.008
AW/NG @ 1800°F	99.990±.004	99.78±.02	99.78±.02
AW/NG @ 1600°F	>99.9975±.0001	99.997±.008	>99.995±.008

NA = Not applicable - No impinger TOC found

TABLE 2-4. INCINERATOR DATA SUMMARY - AVERAGE VALUES FOR EACH SET OF INCINERATOR CONDITIONS

Date	10/22	10/26	10/26*	10/27	10/27	10/27	10/27
Sample Location (1)	RO	RO	RO	RO	WG	RO	WG
<u>Process Data Fuel</u>							
Condition (T)	AW/NG	AW/NG	AW/NG	AW/NG/WG	AW/NG/WG	AW/NG/WG	AW/NG/WG
Incinerator Temp. (°F)	1800	1600	2000	1600	1600	1800	1800
N ₂ Flow (x1000 SCFH)	6.3±0.1	4.8±0.6	5.2	6.25±0.07	6.25±0.07	6.2±0.0	6.2±0.0
Natural Gas Flow (x3500 SCFH)	2.6±0	3.3±0.1	7.5	4.25±0.35	4.25±0.35	5.75±0.07	5.75±0.07
<u>Fixed Gases</u>							
Method 18							
CO ₂ %	5.32±0.14	4.73±0.13	6.75	4.62±0.04	0±0	6.18±0.78	0±0
CO%	0±0	0±0	0	0±0	0±0	0±0	0±0
N ₂ %	87.35±0.30	87.70±0.18	83.0	82.5±0.2	94.83±1.03	82.75±0.57	95.38±0.46
O ₂ %	14.28±0.20	15.03±0.18	12.05	14.98±0.04	1.54±1.21	13.45±0.07	2.08±1.01
<u>Volumetric Flow</u>							
SO Temp. (°F)	126±6	127±0	133	128		132±1.4	
Bar. Pressure ("Hg)	30.4±0.0	30.5±0.0	30.5	30.5		30.5±0.0	
ΔP ("H ₂ O)	0.31±0.00	0.165±0.007	0.15	0.15		0.15±0.00	
Velocity (fps)	33±0	24.5±0.7	23	23		23±0	
ACFM	39200±420	28450±640	27,300	27,200		27,300±0	
SCFM (dry)	30500±710	22050±490	20,400	21,000		20,550±210	
% Moisture	13.5±2.1	14.±0	16	14		15.5±0.7	
<u>Hydrocarbons</u>							
Method 18							
RO (ppm - C ₂ -C ₆)	4.98±2.0	<1.0	1.6	<1.0		<1.0	
WG (vol.% - C ₂ -C ₆)					10±6.3		7.57±0.27
NG (vol.% - CH ₄)							
(vol.% - C ₂ -C ₆)							
<u>Byron 401 ppmv-C)</u>							
THC (w/ascarite)	8.5±3.5	2.2±1.1	2.9	1.4±0.1		1.7±0.6	
THC (wo/ascarite)	98		2.1				
NMHC (w/ascarite)	8.5±3.5	2.1±1.2(2)	1.0	1.55±0.07		1.1±0.5	
NMHC (wo/ascarite)	123		2.1(2)				
CO (w/ascarite)	57±3	<0.5	2.0	6±0		2.7±0.8	
CO (wo/ascarite)	315		0.7				
<u>Method 25</u>							
NMHC	1,230±1390	440±390	1806	143±56		93.8±201	
<u>Speciated HC</u>							
		0.84					

(Continued)

(1) AW - Atactic Waste, NG = Natural Gas, WG = Waste Gas, RO = Waste Heat Boiler Outlet

(2) Difficulties with analysis, value given represents probable concentration.

*Single determination. Therefore, no error limits.

TABLE 2-4. (CONTINUED)

Date Sample Location (1)	10/28 RO	10/28 WG	10/28 RO	10/28 WG	10/29 RO	10/29 WG	10/26,29 NG
Process Data							
Fuel Condition (1)	AH/NG/WG	AH/NG/WG	NG/WG	NG/WG	NG/WG	NG/WG	AH/NG
Incinerator Temp. (°F)	2000	2000	1800	1800	1600	1600	1800±200
N ₂ Flow (x1000 SCFH)	6.05±0.07	6.1±0.0	6.1±0.0	6.1±0.6	4.0±0.0	4.0±0.0	4.8±0.7
Natural Gas Flow (x3500 SCFH)	7.65±0.07	7.65±0.07	>10	>10	9.3±0.0	9.3±0.0	7.4±1.9
Fixed Gases							
Method 18							
CO ₂ %	6.46±0.09	0±0	4.76±0.00	0±0	4.53±0.61	0±0	1.11±0.54
CO%	0±0	0±0	0±0	0±0	0±0	0±0	0±0
N ₂ %	83.55±0.14	93.8±0.7	83.3±0.1	95.18±0.53	82.8±0.8	95.4±0.1	0±0
O ₂ %	11.78±0.18	2.21±0.01	13.4±0.1	0.90±1.12	14.63±0.18	0.31±0.34	0±0
Volumetric Flow							
SO Temp. (°F)	135.5±0.7		135.5±2.1		133.5±0.7		
Bar. Pressure ("Hg)	30.5±0.0		30.5±0.0		30.5±0.0		
ΔP ("H ₂ O)	0.14±0.00		0.125±0.007		0.125±0.007		
Velocity (fps)	22±0		21.5±0.7		21.5±0.7		
ACFM	26,400±0		24,950±640		24900±710		
SCFM (dry)	19,350±210		18,400±850		18,600±570		
% Moisture	17.5±0.7		17±1.4		16±0		
Hydrocarbons							
Method 18							
RO (ppm - C ₂ -C ₆)	<1.0		<1.0		<1.0		
WG (vol.% - C ₂ -C ₆)		10.82±1.33		9.36±1.90		10.83±3.40	
NG (vol.% - CH ₄)							76.2±0.7
(vol.% - C ₂ -C ₆)							9.46±5.11
Byron 401 (ppmv-C)							
THC (w/ascarite)	2.8±0.7		1.1±0.6		0.9±0.4		
THC (wo/ascarite)							
NMHC (w/ascarite)	1.3±0.8		0.7±0.5		0.49±0.02		
NMHC (wo/ascarite)							
CO (w/ascarite)	1.6±2.2		2.3±2.3		1.25±0.02		
CO (wo/ascarite)							
Method 25							
NMHC	69.6±0.2		129±89		143±18		
Speciated HC							
					0.49±.07		

(1) AH - Atactic Waste, NG = Natural Gas, WG = Waste Gas, RO = Waste Heat Boiler Outlet

(2) Difficulties with analysis, value given represents probable concentration.

*Single determination. Therefore, no error limit.

During 10/21 and the first test during 10/22, the VOC content of the Boiler Outlet was much higher than during the rest of the project. This resulted from a process control malfunction of the meter which indicated the ratio between combustion air and quench air. There was not enough combustion air and too much quench air. Many compounds were seen during the on-site hydrocarbon analyses during this upset period. Furthermore, it was observed that the flame color in the incinerator was a dark orange during this period while the flame was a bright yellow during proper operation.

Table 2-4 also presents average values obtained for fixed gas analyses during the various burn conditions. The overall average value for excess oxygen in the boiler outlet was 172%, but as shown below, as the incinerator temperature was increased, the excess oxygen decreased.

<u>Incinerator Temperature</u>	<u>Average Excess O₂ (%)</u>
2000°F	117
1800°F	168
1600°F	212

This occurrence was as expected and demonstrates that with a relatively constant air flow into the incinerator, more oxygen is consumed at higher temperatures (higher fuel rates). Fixed gas analyses of the boiler outlet accounted for approximately 100% of the gases in all tests.

2.3 Composition of Atactic Waste and NO_x Levels

This section contains details on the composition of atactic waste and NO_x levels at the scrubber stack measured during the incinerator tests. These test results are contained in Section 7 of this document.

Atactic waste is the waste resulting from incomplete polymerization. The waste stream also contains spent solvents and catalyst from the

process. The composition and heat value of these wastes are important parameters when considering the feasibility of incineration. The atactic waste was therefore, subjected to ultimate/proximate, Btu/lb and moisture analyses. Table 2-5 presents the average results relative to temperature and fuel conditions. The percentage of carbon in the atactic waste and its heat value (Btu/lb) showed little fluctuation during the testing period. These data show a substantial amount of carbon present in the atactic waste and, consequently, a relatively high heating value associated with it. The low moisture content of the waste also contributes to its high net heat value. Complete results of these analyses are contained in Appendix C.

The results of the NO_x measured at the stack are given in Table 2-6. The highest level of NO_x was reached when the incinerator was tested at 2000°F using AW/NG/WG as the fuel feed. All other NO_x values are the same within two sigma (the 95% confidence interval).

TABLE 2-5. PERCENT CARBON, Btu/LB AND PERCENT MOISTURE IN ATACTIC WASTE
FOR EACH SET OF OPERATING CONDITIONS

Fuel Conditions			Temperature	Percent Carbon	Btu/lb	Percent Moisture
AW	NG	WG				
X	X		1800	76.67 ± 0.79	18848 ± 043	---
X	X		1600	75.81 ± 0.35	18437 ± 057	0.05 ± 0
X	X		2000	75.84 ± 0.19*	18503 ± 003.5*	0.095 ± 0.007*
X	X	X	1600	75.56 ± 0.09	18338 ± 086	0.12**
X	X	X	1800	75.63 ± 0.19	18570 ± 042	0.19 ± 0.028*
X	X	X	2000	75.95 ± 0.35	18656 ± 036	0.30**
OVERALL AVERAGE				75.96 ± 0.56	18576 ± 190	0.13 ± 0.096

*One sample, Two determinations

**One determination

TABLE 2-6. NO_x RESULTS FOR SELECTED INCINERATOR CONDITIONS

INCINERATOR CONDITIONS	NO _x * μg/Nm ³ (ppm)
AW/NG @ 1800°F	6.08E4±4.17E3 (22.33±1.53)
AW/NG @ 1600°F	6.92E4±1.13E4 (25.40±4.16)
AW/NG/WG @ 1600°F	6.60E4±6.05E3 (24.25±2.22)
AW/NG/WG @ 2000°F	1.05E5±8.31E3 (38.6±3.05)
NG/WG @ 1600°F	5.50E4±4.03E3 (20.20±1.48)

*Average includes results from duplicate analyses of identical samples on the same day and repeated analysis of samples on different days.

3.0 PROCESS AND INCINERATION DESCRIPTIONS

The incinerator for this study is located at the ARCO Chemical Company Plant in Deer Park, Texas. To provide a basis for comparison of the operation and efficiency of this incinerator with others as may be required by New Source Performance Standards (NSPS), a brief description of the process and a detailed description of the incinerator follows. The incinerator description includes operational and physical details.

3.1 Process Description

The incinerator and associated waste heat boiler are integral parts of the ARCO Plant. The plant produces "raw" polypropylene which is shipped out for final processing into finished products. The facility actually includes two plants - Monument Plants I and II. The older, Monument I Plant has four polypropylene process trains while Monument II has two process trains. The two plants discharge their wastes to the incinerator system where they are burned. The wastes in the plants occur from:

- processing chemicals and dilution solvents for the catalyst,
- spent catalyst,
- waste polymeric material (atactic waste), and
- nitrogen swept propylene from the final stages of the process.

The feed rates of these wastes to the incinerator vary according to which trains are running and what start-ups are occurring in the two plants. Feed rate variations were observed during the two weeks of the incinerator test.

The waste heat boiler associated with the incinerator provides a major portion of the process steam needed by the two polymer plants. Natural gas is used as an auxiliary fuel to fire the incinerator. If necessary, fuel oil can also be used. Under full production conditions, the atactic waste provides approximately 50% of the energy needed to produce the steam and the natural gas is reduced to a minimum.

3.2 Incinerator Description

The incinerator and associated equipment were designed by John Zink, Incorporated. The system (Model Number SO-083047) was put into operation on August 16, 1978. The incinerator's two main purposes are to destroy organic waste from the polymer processes (primary) and to provide heat to generate steam (secondary).

Figure 3-1 contains a flow diagram of the incinerator and associated equipment. The organic wastes from the Monument I and II Plants are sent to the atactic storage tank. The purge gases are sent directly to the incinerator as shown. To prevent the atactic waste from solidifying in the storage tank and lines, the waste is continuously recirculated (through heat traced lines) to and from the incinerator. A valve in the line between the incinerator and recirculation line regulates the flow of waste into the incinerator. Air and natural gas are also shown in Figure 3-1 entering the incinerator. Each inlet stream has its own nozzle inside the incinerator.

The natural gas is used to start up the incinerator, to maintain a preset temperature and to act as a pilot. Combustion air is fed into the incinerator at the burner nozzles located approximately 4 feet beyond the incinerator entrance. The combustion air flow rate is regulated manually. The quench air enters the incinerator within 3 feet of the burner nozzles. It is used to maintain a constant temperature and provide excess combustion air. The quench air flow rate is automatically controlled by incinerator temperature.

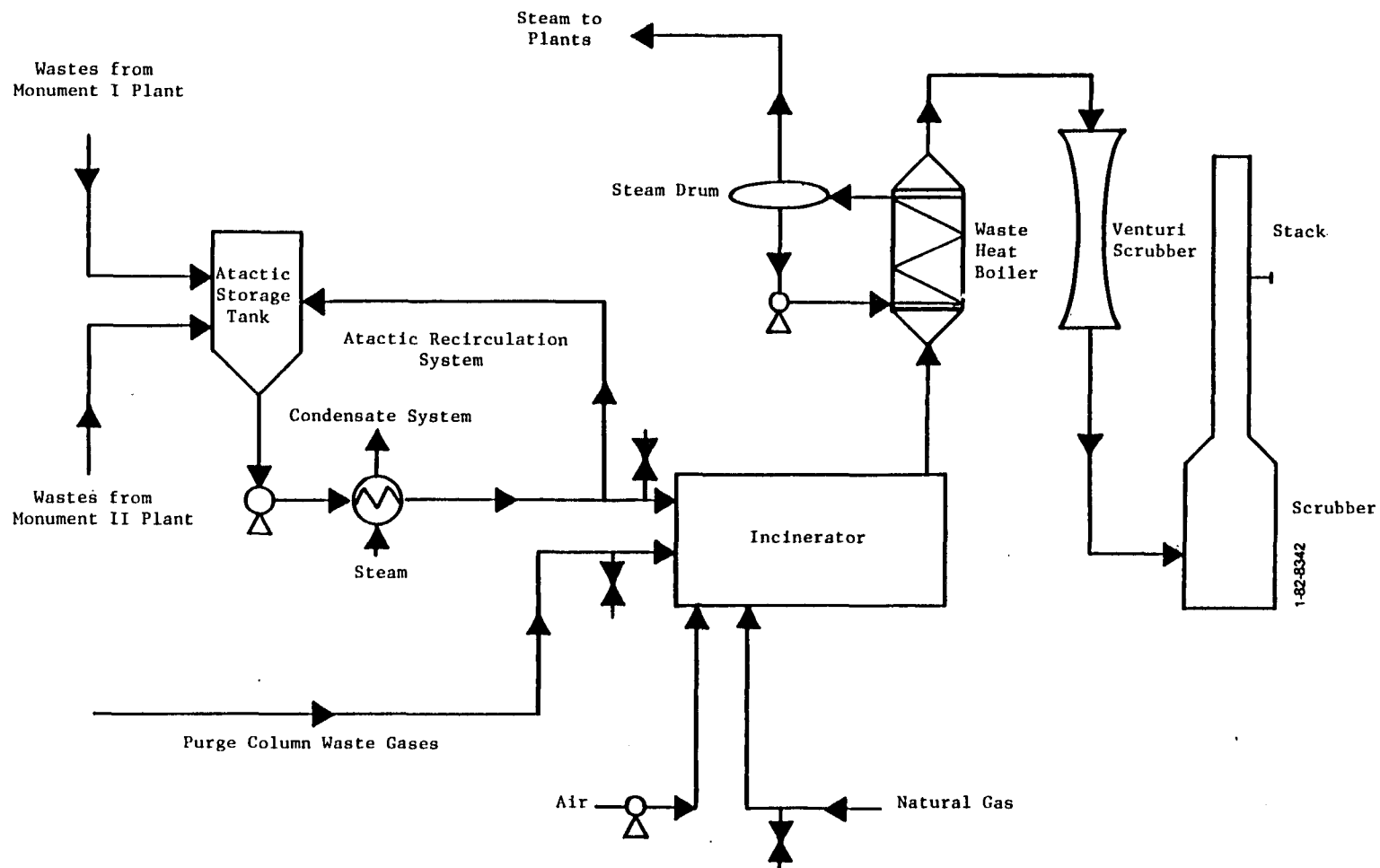


FIGURE 3-1. SCHEMATIC OF INCINERATOR SHOWING INLET AND OUTLET STREAMS

During normal operation with all waste streams entering the incinerator, the natural gas is cut back and the atactic waste becomes the major fuel source. The energy poor purge gas, containing about 95% nitrogen, must always be sent to the incinerator for destruction of the volatile organic carbon (VOC) content since there is no storage facility in the system. During incinerator upset, this stream is sent to a flare.

As the hot gases exit the incinerator, they enter the waste heat boiler where much of the thermal energy is used to produce steam as illustrated in Figure 3-1. The gases then enter a venturi scrubber and are sent to the final caustic cleaning process at the base of the stack.

Figure 3-2 gives the physical dimensions of the system and illustrates the downstream components associated with the incinerator. The sampling point at the top of the waste heat boiler was used to obtain all gaseous samples for VOC analyses after incineration. However, this point could not be used to obtain flowrate measurements due to obstructions in the waste heat boiler. The volumetric flowrate, therefore, was determined on the stack where the Environmental Protection Agency stack sampling criteria were met.

ARCO Chemical Company provided data to illustrate normal operating parameters for the incinerator. These are listed in Table 3-1 and represent the average of the parameters for the month of August, 1981. The following are considered design parameters:

- 7.45 MM Btu/hr,
- air supply \cong 33,900 SCFM
- firebox temperature \cong 1800°F (2200°F maximum),
- firebox residence time \cong 1.5 seconds, and
- pressure \cong 78" H₂O .

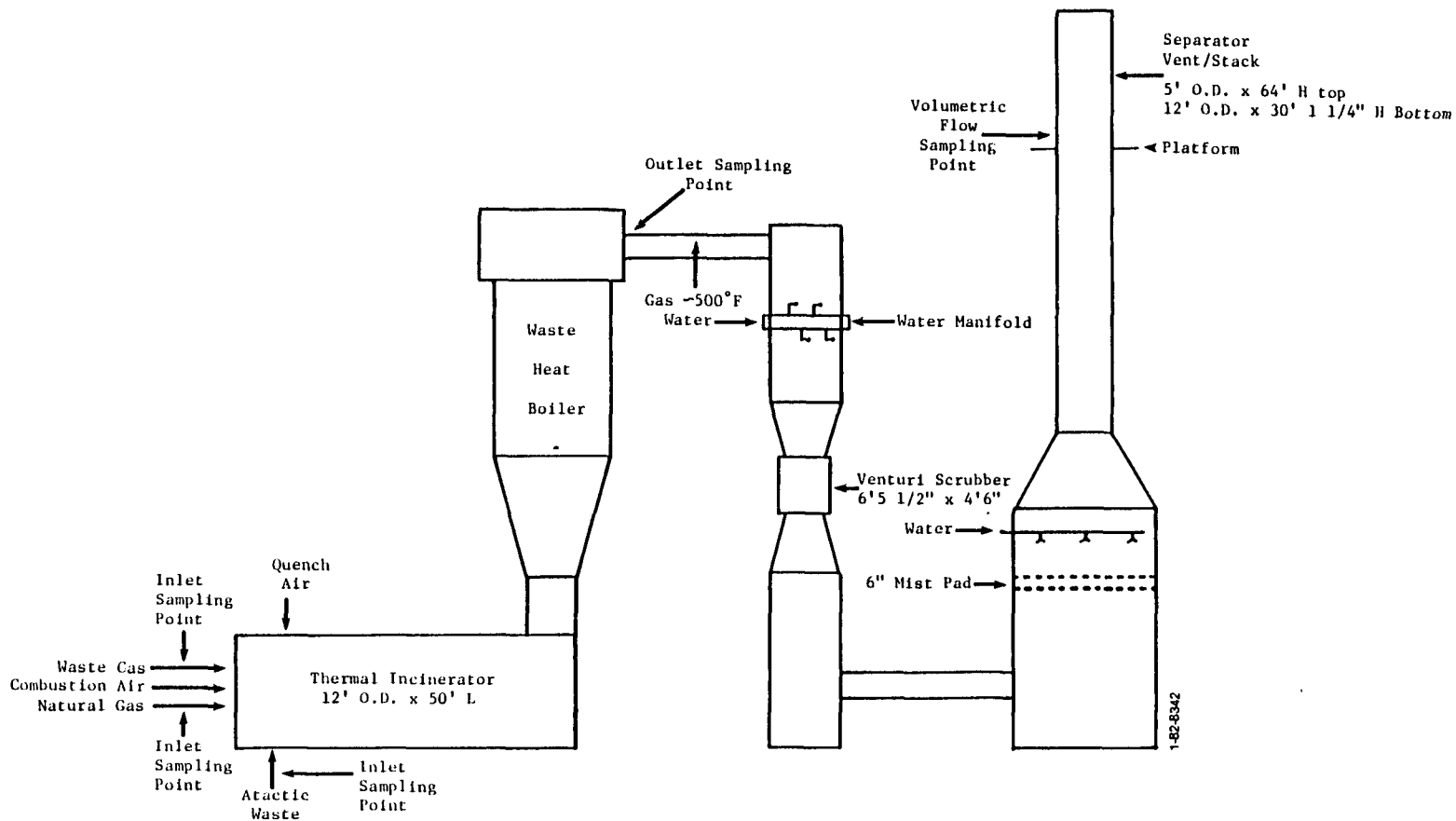


Figure 3-2. Incinerator System with Dimensions

TABLE 3-1. TYPICAL INCINERATOR PARAMETERS BASED ON DATA FROM AUGUST, 1981
(PROVIDED BY ARCO CHEMICAL COMPANY FROM PROCESS DATA)

Parameter	Monument I Plant -Waste Liquid-	Monument II Plant -Waste Liquid-	Purge Column Gas -Waste Gas to Incinerator-	Atactic Waste -Recirculation-
Temperature: Average	-	-	-	-
Range	60-68°C(140-155°F)	52-60°C(125-140°F)	107-116°C(225-240°F)	66-71°C(150-160°F)
Pressure: Average	-	-	-	585kPa(85psig)
Range	960-1,030kPa(140-150psig)	998-1,070kPa(145-155psig)	21-41kPa(3-6psig)	-
Maximum	-	-	-	860kPa(125psig)
Steam Rate: Average	-	-	0	-
Maximum	-	-	-	-
Air Flow: Average	-	-	-	-
Maximum	-	-	-	-
Nitrogen Flow: Range	-	-	0.047-0.062m ³ /sec(6,000-8,000scfh)	-
Organic Solids: Average	41.2g/sec(327Lb/hr)	51.8g/sec(411Lb/hr)	-	-
Organic Liquids: Average	32.7g/sec(259Lb/hr)	32.7g/sec(259Lb/hr)	-	~126g/sec(~1,000Lb/hr)
Organic Gases: Average	3.9g/sec(31Lb/hr)	4.4g/sec(35Lb/hr)	-	-
Range	-	-	11-13g/sec(90-100Lb/hr) (propylene)	-

TABLE 3-1. (CONTINUED)

Parameter	Atactic Waste		Air to Incinerator		Natural Gas*		Steam Production		Waste Heat Boiler Outlet	
	-Incinerator Inlet-		-Combustion and Quench-		-Incinerator Inlet-		-From Waste Heat Boiler-		-VOC Sampling Point-	
Temperature: Average	-	-	41°C(105°F)	-	29°C(85°F)	-	193°C(380°F)	-	211°C(412°F)	-
Range	66-68°C(150-155°F)	-	-	-	-	-	-	-	-	-
Pressure: Average	413kPa(60psig)	-	-	-	-	-	1,240kPa(180psig)	-	-	-
Range	-	-	-	-	34-69kPa(5-10psig)	-	-	-	8.5-18kPa(34-71"H ₂ O)**	-
Maximum	-	-	-	-	-	-	-	-	-	-
Steam Rate: Average	-	-	-	-	-	-	3,250g/sec(25,800Lb/hr)	-	-	-
Maximum	-	-	-	-	-	-	6,680g/sec(53,000Lb/hr)	-	-	-
Air Flow: Average	-	-	11.34m ³ /sec(24,000scfm)	-	-	-	-	-	-	-
Maximum	-	-	16.02m ³ /sec(34,000scfm)	-	-	-	-	-	-	-
Nitrogen Flow: Range	-	-	-	-	-	-	-	-	-	-
Organic Solids: Average	-	-	-	-	-	-	-	-	-	-
Organic Liquids: Average	-	-	-	-	-	-	-	-	-	-
Organic Gases: Average	-	-	-	-	-	-	-	-	-	-
Range	-	-	-	-	0.079-0.118m ³ /sec (10,000-15,000scfh) (Cut back during Atactic Waste incineration)	-	-	-	-	-

* #6 Fuel oil can be substituted for natural gas.

** During test period, this pressure was ~10" H₂O.

4.0 SAMPLING METHODOLOGY

This section describes the sampling procedures and sampling locations used to determine the VOC destruction efficiency of ARCO Chemical Company's Monument II incinerator. Typically, referenced methods were used in this program. In situations where a non-referenced method or modifications of referenced methods were used, documentation of the specific technique(s) is presented. Schematic diagrams of each sampling system are also included in this section.

4.1 Description of Sampling Points

To characterize the VOC destruction efficiency across the thermal incinerator, liquid, solid, and gas phase sampling was performed. Figure 4-1 is a schematic of the incinerator process with the five sampling locations indicated. These locations were:

- Incinerator Inlet
 - 1. Waste gas stream,
 - 2. Natural gas stream,
 - 3. Atactic waste stream,
- Waste Heat Boiler Outlet, and
- Scrubber Stack Outlet.

4.1.1 Incinerator Inlet

The incinerator inlet consists of the following three individual process streams;

- Waste gas,

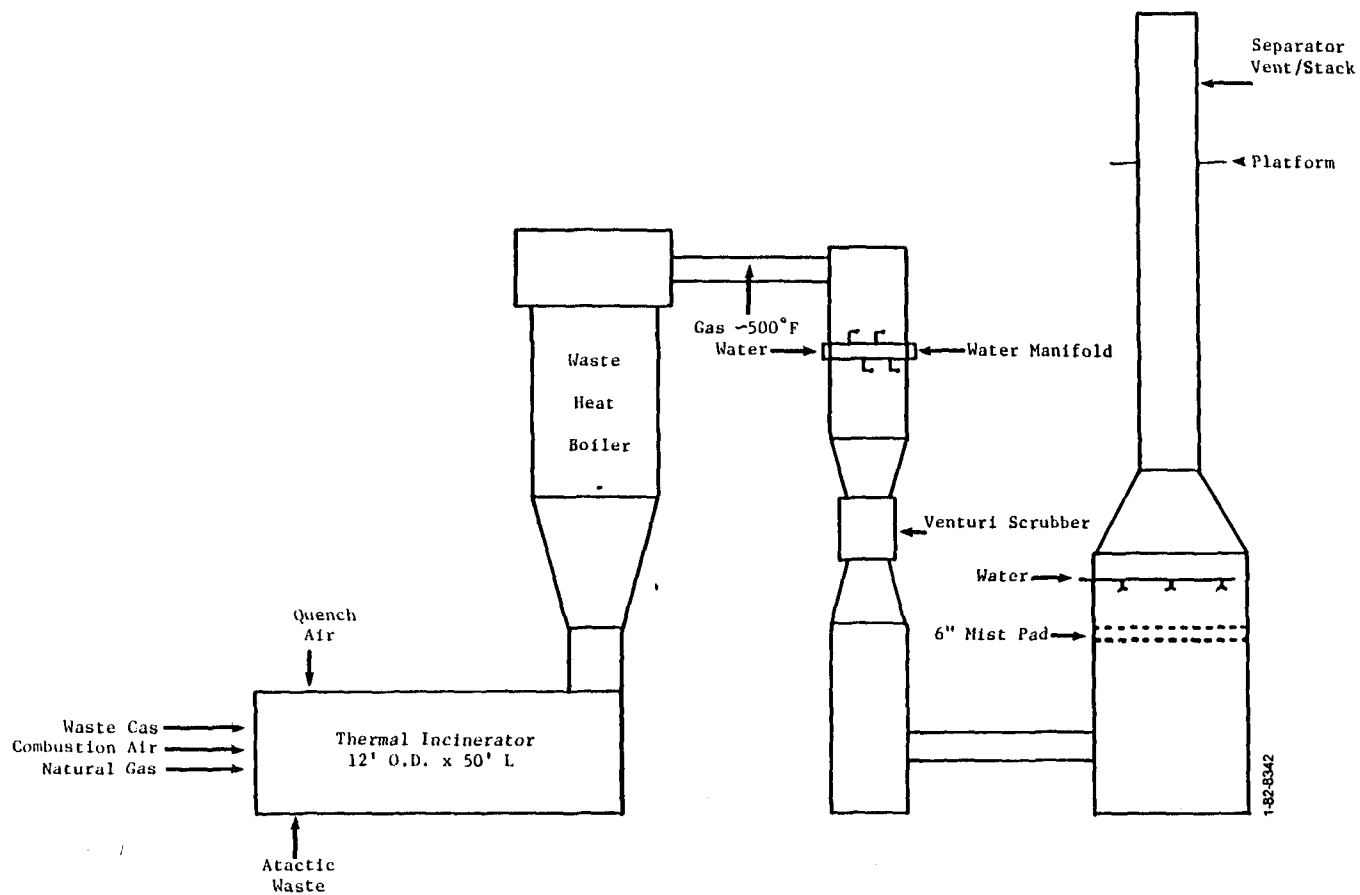


Figure 4-1. Incinerator System with Sampling Point Locations

- Natural gas, and
- Atactic waste streams.

Figure 4-1 shows that the three sampling points are located just before the three streams enter the incinerator.

4.1.2 Waste Heat Boiler Outlet

Figure 4-1 also shows the location of the sampling point for the incinerator waste heat boiler. A half inch stainless steel tube exiting the waste heat boiler was heat traced and maintained at a temperature of ~250°F. Samples were collected simultaneously by the Byron 90, Method 25, and proposed Method 18 procedures. The temperature of the flue gas exiting the waste heat boiler ranged from 420°F to 450°F and gas pressure ranged from 8 to 12 inches of water.

4.1.3 Scrubber Stack Outlet

Due to the physical constraints of the process ducting, volumetric flow rate determinations for the flue gas exiting the incinerator were not made at the exit of the waste heat boiler. Flow rate determinations were instead performed at the incinerator's scrubber stack outlet where sampling points meeting EPA criteria are located. These sampling points, two four inch ports positioned at 90 degrees to each other, provided access to the flue gas.

4.2 Volatile Organic Carbon Sampling Methods

4.2.1 EPA Method 25

EPA Method 25 (1) provided a means for determining total gaseous

nonmethane organic emissions as carbon. It is applicable to measuring volatile organic carbon (VOC) as total gaseous nonmethane organics (TGNMO). Organic particulates, if present, interfere with the analysis and were consequently removed with a filter.

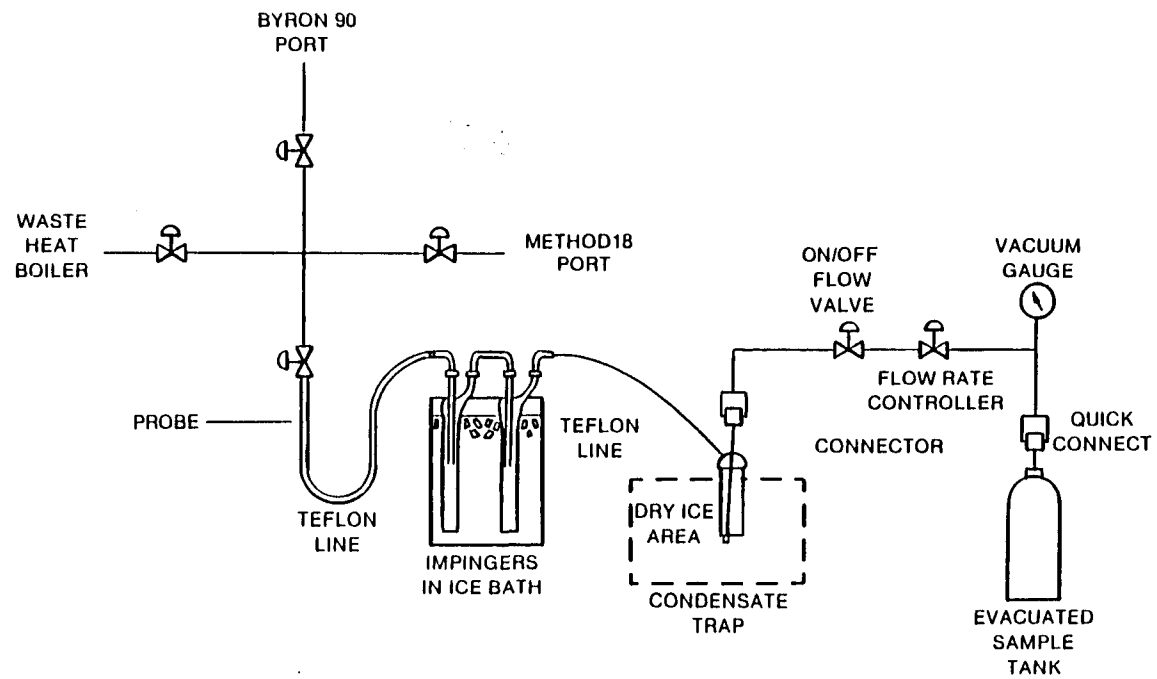
All Method 25 sampling was subcontracted to Pollution Control Science, Inc., and was performed using personnel and equipment supplied by the subcontractor.

The sampling system used for Method 25 consisted of a mini-impinger moisture knockout, a condensate trap, a flow control system, and a sample tank. This is depicted in Figure 4-2. Initially, the entire probe, trap, and tank system were leak-tested to ensure sample integrity. Sampling was accomplished by evacuating the tank, inserting the probe in the waste heat boiler port, adjusting the flow to maintain a constant flow into the tank, and monitoring the time until constant flow could no longer be maintained or until sufficient sample had been collected. A post-sampling leak test was then performed. Lighter VOC components were separated into the gas phase in the tank and the heavier components were condensed in the trap along with water vapor if it had not been removed upstream. A more complete description of this method is found in Appendix E.

4.2.2 Proposed EPA Method 18

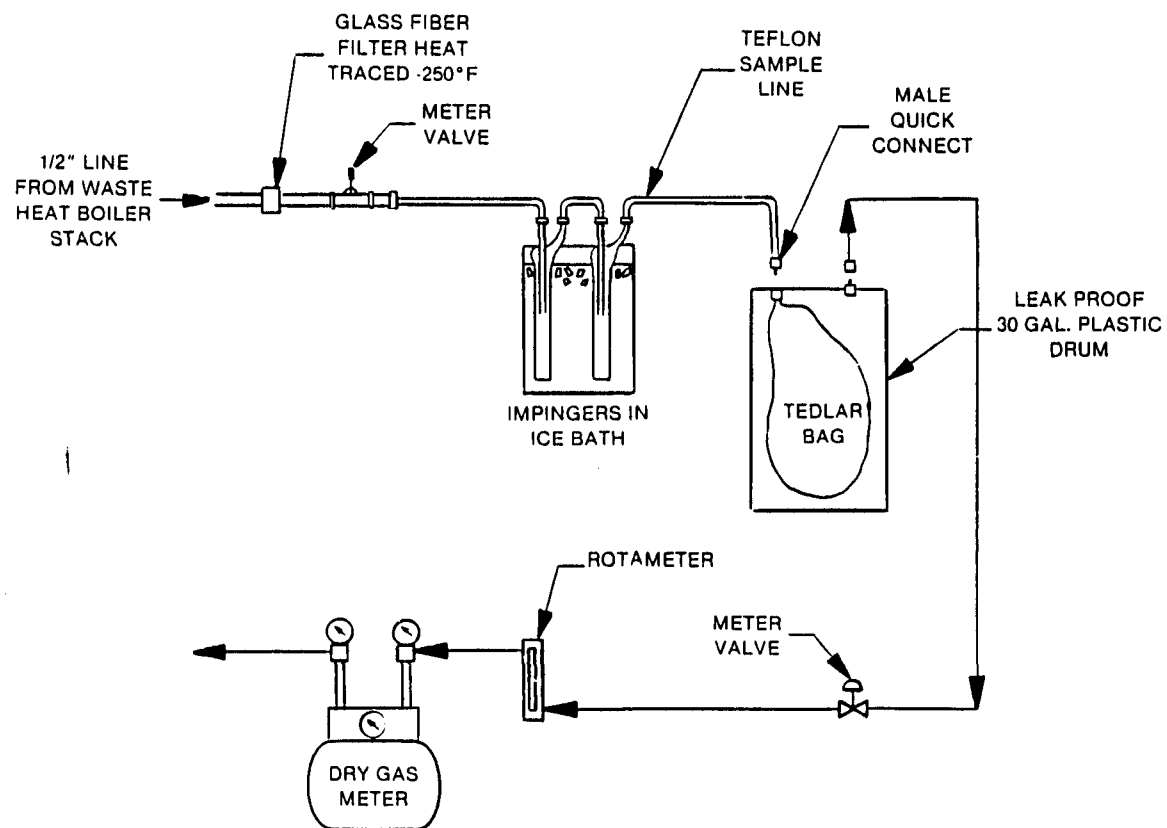
The following section discusses the procedures which were used to collect samples of organics following the proposed EPA Method 18 (2). It also includes a discussion of method validation. Samples were collected using a modification of EPA Method 110 (3) for benzene which is also included in the proposed EPA Method 18. This modification was necessary due to the high moisture content of the incinerator gases and the positive pressure of the emissions.

Figure 4-3 illustrates the sampling train used to collect samples



70A2330

Figure 4-2. Method 25 Sample Acquisition Apparatus



70A2331

Figure 4-3. EPA Proposed Method 18 Sampling Apparatus

from the Waste Heat Boiler stack. There are three differences between this system and the one proposed in Method 18. These are:

- a glass fiber filter for particulate removal,
- a metering valve to regulate flow due to pressure from the stack, and
- a set of two modified impingers in an ice bath to condense out moisture.

To ensure that a representative, integrated sample was collected using the modified Method 18 shown in Figure 4-3, three validation tests for sample flow rate and sample volume into the Tedlar bag were performed. These tests were performed by inserting a rotameter and dry gas meter into the sampling system at points both before and after the Tedlar collection bag. Sample flow rates and sample volumes into the Tedlar bag were compared to the flow rates and volumes of air displaced from the collection bag's leak-proof container. For all three tests both flow rates and total volumes agreed within $\pm 5\%$. Also, three comparisons for total volume collected in the Tedlar bags were made. This was done by totally evacuating three bags and monitoring the evacuated volume with a dry gas meter. These volumes were compared to the gas volumes obtained for each bag when the bags were filled according to sampling procedures. The agreement was within $\pm 3\%$.

Gas samples of the waste gas stream were also obtained using the Method 18 sampling procedure. Samples were obtained from the waste gas stream without a pump since the stream was under sufficient positive pressure for passive collection. Also, the filter was omitted at this location since particulates were not present.

4.2.3 Byron Method

Byron Instruments produces a Model 401 analyzer which, when used in conjunction with their Model 90 sample collector and Model 75 converter, is capable of performing analyses similar to EPA Method 25. Sampling with the Byron Method is outlined below. The analytical technique is discussed in Section 5.

The principle underlying this method is the same as EPA Method 25. However, rather than using a modified standard GC, the Byron Method uses a process analyzer. This instrument speciates C_2 from higher hydrocarbons, but gives a single value for all nonmethane hydrocarbons. After separation, all carbonaceous material is combusted to CO_2 which is then converted to CH_4 before being measured by an FID. Thus, the variable response of the FID to different types of organics is eliminated in the Byron 401 as it is in EPA Method 25.

The Byron 90 sampling system has the following components:

- fiberglass filter plug,
- 1/4" stainless steel probe,
- mini-impinger moisture knockout,
- Teflon sample lines,
- trap for heavy organics,
- pump, and
- mass flowmeter and Tedlar collection bag.

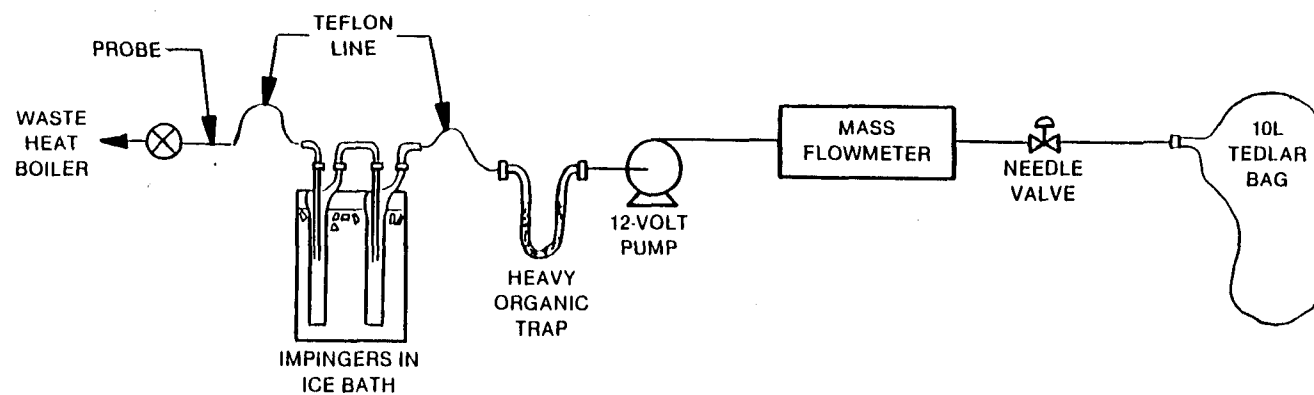
A schematic diagram of this sampling train is depicted in Figure 4-4.

Prior to sampling, the filter, probe, moisture knockout, trap, pump, and bag system were leak tested. During sampling the probe was installed and the sample was allowed to flow through the Model 90 system. Due to sufficient gas pressure the pump was not needed. A one-hour integrated sample was collected at a constant flow rate between 100-120 cc/min. At the end of the sampling hour, the 10-liter Tedlar bag contained CH_4 , CO, CO_2 , water vapor, and other light organics not removed by the heavy organic trap. Due to blank problems encountered with the heavy organics trap, it was eliminated during most of the testing. These problems are discussed further in Appendix D.

When the heavy organics trap was used, the trapped organics were recovered through the use of a modified Byron 75 conversion unit. The organic trap was attached to the unit and a small volume of zero air was blown through to remove entrained CO_2 . A volume of carrier gas equivalent to the original sample volume was then passed through the trap while the trap was heated to a dull red. The remobilized organics were directed over a catalyst and converted to CO_2 before being collected in another 10-liter bag. Flow into the bag was measured using a digital mass flowmeter. Thus, at the end of this phase of the analysis, the sample had been split into two 10-liter Tedlar bags, each containing the same volume of gas. The original gas contained non-trapped VOC, CO_2 , CO, and any water vapor from the sample. The second bag contained the CO_2 obtained from oxidizing all of the trapped organics.

4.3 NO_x Sampling at Waste Heat Boiler Stack

The oxides of nitrogen (NO_x) content of the flue gas was determined using the methodology specified in EPA Method 7 (1). Based on this method, triplicate grab samples of the flue gas were collected in evacuated



70A2312

Figure 4-4. Schematic Diagram of Byron Sample Acquisition Apparatus

flasks that contained a dilute sulfuric acid-hydrogen peroxide solution. An illustration of the NO_x sampling train is presented in Figure 4-5.

4.4 Scrubber Stack Volumetric Flow Rate

The total gas flow rate was determined two or three times daily using procedures described in EPA Method 2 (1). Based on this method, the volumetric gas flow rate was determined by measuring the cross-sectional area of the stack and the average velocity of the flue gas. The area of the stack was determined by direct measurements.

The average gas velocity was calculated from the average gas velocity pressure (measured by the pressure differential across the pitot - ΔP), the average flue gas temperature, the absolute static pressures, and the wet molecular weight determined from EPA Method 3 (1) and 4 (1) (Section 4.5). Pressure and temperature profile data was obtained by traversing both diagonals of the stack. The number of sampling points required to statistically measure the average gas velocity was determined using the procedures outlined in EPA Method 1. The number of sampling points and their distance from the duct wall is a function of the proximity of the sampling location to its nearest upstream and downstream flow disturbance.

ΔP and temperature profile data were measured at each of the sampling points using an S-type pitot and K-type thermocouple. A Magnahelic gauge of the proper range was used to measure the pressure drop (ΔP) across the S-type pitot. A barometer was used to obtain the barometric pressure at least twice daily. The static gas pressure at the scrubber outlet was measured by disconnecting one side of the S-type pitot and then rotating the pitot so that it was perpendicular to the gas flow. A Magnahelic gauge attached to the S-type pitot measured the static pressure within the duct.

4.5 Flue Gas Molecular Weight and Flue Gas Moisture

The dry and the wet molecular weight of the flue gas were

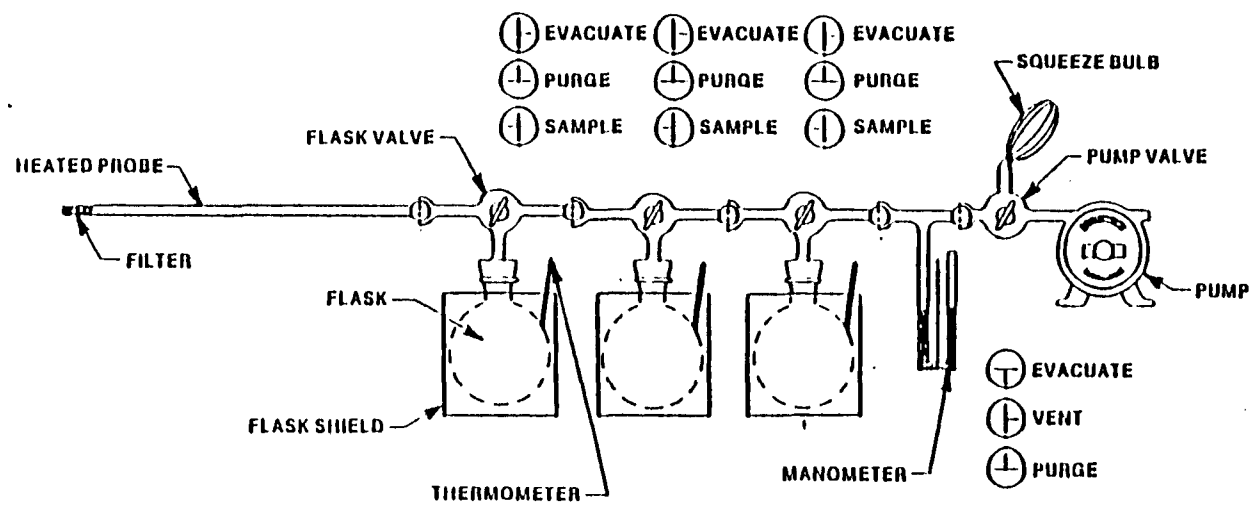


Figure 4-5. EPA Method 7 - NO_x Sampling Train

calculated using data from the fixed gas analyses of the Method 18 samples and from the scrubber stack moisture determinations. The method for calculating flue gas molecular weight is described in EPA Method 3. The moisture content of the scrubber stack gas was obtained from a psychometric chart once the moisture was determined to be at the saturated level.

4.6 Atactic Waste Sampling

The atactic waste is a combination of gaseous and semisolid wastes from the polypropylene process. There are two plants at the facility which produce this waste. The atactic (unsymmetrical polymeric) waste is piped from these two plants through heat-traced lines to a heated surge tank where the pressure is reduced to about 60 psig by venting excess gases to a flare. The atactic waste is then pumped to the incinerator in a continuous, heated loop to prevent solidification. A portion of the waste enters the incinerator while the rest recirculates to the surge tank. No process flow measuring devices are present in any part of the atactic waste system.

Samples of the atactic waste were obtained from an on/off valve in the heated loop just before the incinerator. The valve had two feet of flexible stainless steel pipe (1") onto which the sampling vessels were attached. Since samples of the gas as well as the semisolid were required, a special apparatus was prepared for this purpose as illustrated schematically in Figure 4-6. After connecting the sampling vessel to the flexible stainless steel tube, the atactic waste feedline was purged through the sample purge valve shown in Figure 4-6. After 4 to 6 seconds the purge valve was closed and the on/off valve to the sampling device was opened slowly to allow approximately 200 to 500 grams of sample to be collected. The necessary collection time was determined by trial and error. Both valves were then closed and the sample purge valve opened to relieve line pressure in the one-inch tube.

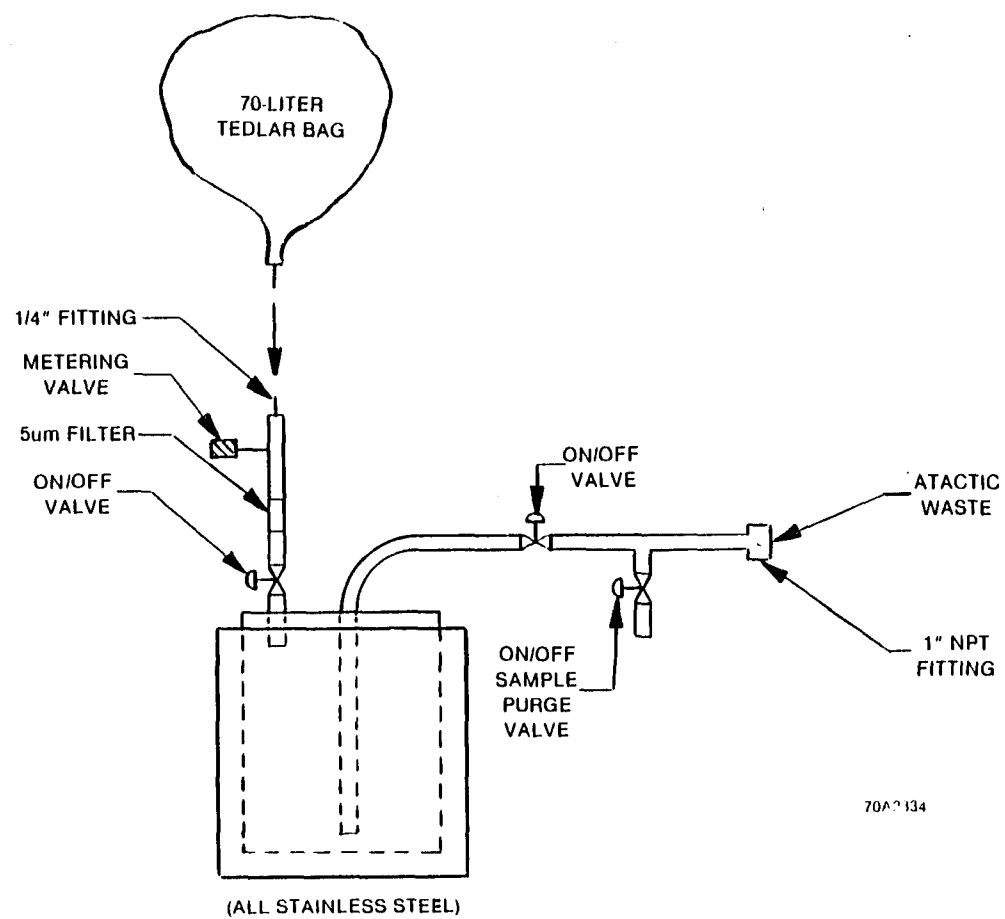


Figure 4-6. Atactic Waste Sampling Bomb

The sampling device was then brought to the mobile laboratory and weighed. To determine if dissolved gases were present in the atactic waste, any off-gases were vented through the metering valve into a clean Tedlar bag. Visual observation of the bags following gas collection and reweighing of the sampling device after venting indicated little if any gas being vented. An attempt to collect the vent gas sample immediately following collection of the atactic waste sample resulted in a large amount of the atactic solid/liquid phase being vented into the Tedlar bag.

4.7 Waste Gas Stream

The sampling procedure used for the waste gas stream was again a modification of EPA Method 110. This methodology was described in Section 4.2.2 and the proposed sampling train is illustrated in Figure 4-3. Due to the high moisture content of this stream, the impinger-condenser system was used. Since particulates were not a problem in this stream, the in-line glass fiber filter was not used. A sampling pump was not necessary since the line pressure (2 psig) was sufficient to collect an integrated sample. Metering valves and a rotameter were used to control the sampling flow rate.

4.8 Natural Gas

Since the composition of ARCO's natural gas feed stream proved to be constant, only grab samples were collected for analysis. The grab samples were passively collected in 70 liter Tedlar bags since line pressures of approximately 3 psig allowed sample acquisition without a pump.

4.9 Miscellaneous Readings

In addition to the streams described above, other streams were monitored to determine inlet loadings and outlet emission rates. During

testing periods process information was collected for:

- Nitrogen flow rate,
- Steam production rate,
- Propylene usage rate,
- Polypropylene production rate,
- Natural gas flows,
- Atactic surge tank levels, and
- Incinerator temperature.

A complete list of process information is given in Appendix B.

5.0 ANALYTICAL METHODOLOGY

5.1 Gas Analysis

During the testing phase of this program three different methods were used for the collection and analysis of hydrocarbons. These were:

- 1) Proposed EPA Method 18,
- 2) Byron Method, and
- 3) Method 25.

In addition to hydrocarbon data, the proposed Method 18 samples were also analyzed for fixed gases and speciated for hydrocarbons.

5.1.1 Proposed Method 18 for Hydrocarbons

Light hydrocarbons (C_1-C_6) and heavy hydrocarbons (C_7+) were determined on-site under the following conditions:

Instrument: Antek Model 460 GC-FID

Column: 1.8 m x 3.2 mm O.D. stainless steel; Porapak Q
80/100 mesh

Carrier: Nitrogen at 40 mL/min

Oven Program: 40°C for 2 min; 10°C/min to 160°C;
160°C for 12 min

Backflush: 20 min

Integrator: Hewlett-Packard 3390A

Gas samples were introduced into the instrument through 100 μ L, 1 mL or 5 mL sample loops which had been flushed 100-fold with sample. After the C₁-C₆ components had eluted, the column was backflushed to obtain the C₇+ compounds. Chromatograms were integrated using a Hewlett-Packard 3390A integrator. All eluted peaks were then quantitated against certified propane standards.

To ensure data quality, daily calibrations of the instrument were performed. A one point calibration with certified propane standard was used for quantification and a C₁-C₇ normal hydrocarbon mixture was used daily to update retention times. Once the instrument was calibrated, a quality control (QC) standard was analyzed. The values for the QC standard were always well within the acceptance criteria of $\pm 20\%$ of the average value for the standard (See Section 6.0).

The following discussion illustrates the conversion of peak areas to carbon mass per volume. First, the response factor (RF) for ppmv-C was calculated from the daily calibration as follows:

$$\begin{aligned} \text{RF} &= \frac{\text{Peak Area from Propane Standard}}{\text{Certified ppmv-propane} \times 3 \text{ Carbon atoms/propane molecule}} \\ &= \text{Area/ppmv-C} \end{aligned}$$

When a sample was analyzed the peak areas of interest were summed (e.g., ΣC_4 TO C₅). The resulting area was then divided by the RF:

$$\text{ppmv-C/Species of Interest} = \frac{\text{Area(s) of Species of Interest}}{\text{RF (Area/ppmv-C)}}$$

Finally, to convert ppmv-C to carbon mass per unit volume (using pounds per standard cubic foot as an example) the following equation was used:

$$\text{lbs C/SCF} = \frac{\text{ppmv-C (Species of Interest)}}{\frac{10^6 \text{ ppmv/Unit Volume}}{0.8493 \text{ ft}^3/\text{mole}^*}} \times \frac{12 \text{ g/mole}}{454 \text{ g/lb}}$$

* at 68°F and 29.92" Hg

where SCF is defined as standard cubic feet at 68°F and 29.92" Hg.

To obtain mass per unit time (e.g., lbs C/hr), the flow rate (e.g., SCF/hr) of the stream at 68°F and 29.92" Hg was multiplied by mass per unit volume (lbs C/SCF).

Mass Flow (lbs/hr) = Flowrate (SCF/hr) x Mass per Unit Volume (lbs C/SCF)

5.1.2 Byron Total Hydrocarbon Analyzer

During the on-site testing the Byron Model 401 Total Hydrocarbon Analyzer was operated in its "full cycle" mode, producing data for total hydrocarbons, non-methane hydrocarbons, carbon dioxide, methane and carbon monoxide. Analysis of the gas sample was accomplished by first separating the carbonaceous compounds in a series of chromatographic columns. These hydrocarbons were then passed separately through a catalytic oxidizer where they were oxidized to CO₂ then through a catalytic reducer where they were reduced to methane. A flame ionization detector (FID) measured the resulting methane. An initial instrument calibration was run using a series of three standards of varying concentrations. A daily standard was run to determine the daily response factor of each compound and to ensure that the instrument response had not drifted more than 10% from the 3-point calibration. Appendix D contains more information concerning this analytical method.

5.1.3 Volatile Organic Compounds (VOC's) - EPA Method 25

Each Method 25 sampling run yielded 2 sample fractions which were analyzed separately for VOC's.

- The chilled condensate trap contained organics which were oxidized to CO_2 and quantitatively collected in an evacuated vessel. An aliquot of the CO_2 was then reduced to CH_4 and quantitated using an FID.
- The sample tank was also analyzed for volatile organics. An aliquot from the tank was injected into a gas chromatographic column to achieve separation of the non-methane organics from CO , CO_2 and CH_4 . These compounds were then oxidized to CO_2 , reduced to CH_4 and determined by FID.

The results from both sample fractions were then totalled to yield the total gaseous nonmethane organics (TGNMO) present in the sample. Appendix E contains a detailed description of Method 25 as performed by Pollution Control Sciences, Incorporated.

5.1.4 Hydrocarbon Speciation

Samples of the boiler outlet gas were sent back to Radian and analyzed for low level hydrocarbon species. This was accomplished under the following conditions:

Instrument: Varian Model 3700 GC-dual FID

Column 1: 6 m x 1.6 mm O.D. stainless steel micropacked;
n-octane on Porasil C, 100/120 mesh (used for
 $\text{C}_2\text{-C}_5$ analysis)

Carrier 1: Nitrogen at 7 mL/min

Column 2: 60m x 0.32mm I.D. fused silica capillary;
SE-30 (used for C₅-C₁₀ analysis)

Carrier 2: Helium at 2 mL/min

FID Make-up: Nitrogen at 30 mL/min

Oven Program: -50°C for 2 min; 6°C/min to 80°C;
80°C for 20 min

Integrator: Varian Vista 401 chromatographic data system

To attain the desired detection levels, immediately prior to analysis, gas samples were concentrated in 2 cryogenic traps. The samples were then desorbed onto the head of each chromatographic column and analyzed according to the above conditions. All peaks were quantitated against propane standards (for C₂-C₅) or hexane standards (for C₅-C₁₀). A detailed description of this chromatographic system which was interfaced with a computerized data center is given in Appendix F.

5.1.5 Fixed Gases

The on-site fixed gas analyses were performed under the following conditions:

Instrument: Fisher Gas Partitioner Model 1200 GC-TCD

Column 1: 2m x 3.1mm; Porapak PQ

Column 2: 3.4m x 4.8mm; Molecular Sieve 13X

Carrier: Helium at 30 mL/min

Oven Temp: 50°C

Bridge Current: 275 mA

The instrument was calibrated using 3 sets of certified standards at varying concentrations. Additional standards were also run daily to ensure that the instrument calibration had not drifted. Peaks were recorded on a chart recorder and quantitated against standards using peak height measurements.

5.1.6 NO_x

Samples obtained from the Method 7 NO_x runs were analyzed according to the EPA methods contained in Reference 1. In this procedure, the nitrogen oxides (except nitrous oxide) are collected and oxidized to nitrate in a sulfuric acid-hydrogen peroxide absorbing solution. Following the pH adjustment using ammonium hydroxide, all samples were filtered to remove the resulting solids. The yellow compound which results from the reaction of nitrate and phenoldisulfonic acid is measured colorimetrically at 400 nm and quantitated against a calibration curve as NO_x.

5.1.7 BGI Filters

The BGI filters used to remove entrained particulate were prepared for analysis by soxhlet extracting the filters for 24 hours with methylene chloride, then concentrating the methylene chloride extract to 2 mL. The extracts were analyzed for total chromatographable organics (TCO) and the gravimetric residue after evaporation (GRAV) (Ref. 4). These analyses provide a quantitation of the amount of extractable organic material in the sample. The TCO method quantitates organics in the 100°-300°C boiling range and the GRAV value represents organics with a boiling point greater than 300°C.

Extracts were analyzed for TCO under the following conditions:

Instrument: Tracor Model 560 GC-FID

Column: 3.05m x 2mm, I.D. glass; 10% OV-101 on
100/120 Supelcoport

Oven Program: 50°C for 5 min; 20°C/min to 250°C;
250°C for 15 min

Carrier: Nitrogen at 40 mL/min

Injector Temp: 200°C

Detector Temp: 300°C

Chromatograms were quantitated against a C₈, C₁₂, C₁₆ n-paraffin standard using a Hewlett Packard 3380A integrator.

GRAV analyses were performed by evaporating 1 mL of each extract at room temperature and weighing to a constant weight (± 0.1 mg) on a Mettler H35AR four place balance.

5.2 Aqueous Condensate Analysis

Aqueous condensate samples collected from the proposed Method 18 impingers were analyzed for total organic carbon content (TOC). Selected samples of this condensate were characterized for various inorganic species instead of TOC.

5.2.1 Total Organic Carbon (TOC)

Total organic carbon was determined according to EPA Method 415.1 using a Beckman Model 915A Total Organic Carbon Analyzer. Carbonaceous material in the samples was converted to CO₂ by catalytic combustion. The CO₂ formed was measured by a nondispersive infrared detector. Prior to analysis, inorganic carbon (HCO₃⁻, CO₃⁼) was removed by acidification and sparging with nitrogen.

5.2.2 Inorganic Species

Table 5-1 below gives the methods used to determine the inorganic species. In each case the referenced procedures are identical except where modifications are noted.

TABLE 5-1. METHODS USED TO DETERMINE THE INORGANIC SPECIES

	<u>EPA</u> ¹	<u>STANDARD METHODS</u> ²	<u>ASTM</u> ³
TOC	415.1	505	D2579-74
pH	150.1	402	D1293-65
TSS	160.1	209D	D1888-67
PO ₄ ³⁻	365.2	(424F 424C-III Digestion)	D515-72, Method A
SO ₄ ²⁻	375.4	426C	D516-68, Method B
ACIDITY	305.1	(402)*	D1067-70, Method B*
ALKALINITY	310.1	403	D1067-70, Method B
Cl ⁻	325.3	407B	D512-67, Method A
F ⁻	(340.2)**	(413B)**	(D1179-72, Method B)**
NO ₃ ⁻ †	-	418B	-
NO ₂ ⁻	354.1	419	D1254-67

¹ EPA, Methods for Chemical Analysis of Water and Wastes, EPA-600 4-79-020 U.S. EPA, Cincinnati, Ohio, March 1979.

² Standard Methods for Examination of Water and Wastewater, 15th Edition, APHA, AWWA, and WPCF, 1981.

³ Annual Book of ASTM Standards, Water, 1977, American Society for Testing and Materials, Philadelphia, PA, 1977.

* plus H₂O₂ digestion

** Ion selective electrode using standards addition instead of a calibration curve.

† Chromatropic acid

5.3 Atactic Waste Analysis

5.3.1 Ultimate, Proximate, Btu Content

The ultimate, proximate and Btu content of the atactic waste were determined according to the following ASTM methods:

<u>Analysis</u>	<u>ASTM Method Number</u>
Ultimate	D3176-74
Proximate	D3172-73
Btu content	D3286-77

5.3.2 Moisture

The weight percent moisture in the atactic waste was obtained by Karl Fischer titration, following ASTM Method D-1744.

6.0 QUALITY ASSURANCE

The work performed during this program incorporated a comprehensive quality assurance/quality control (QA/QC) program as an integral part of the overall sampling and analytical effort. The major objective of the QA/QC program was to provide data of known quality with respect to:

- completeness,
- accuracy,
- precision,
- representativeness, and
- comparability.

The quality assurance function was organized to provide independent review and assessment of project activities and ability to achieve the stated data quality objectives. The QA coordinator for the project had the responsibility of evaluating the adequacy and effectiveness of the QC system and providing assurance that it was, in fact, responsive to the specific needs of the program.

While the system of QA activities was necessarily independent of the technical effort per se, the QC system was an integral part of the daily technical effort. It was designed to provide an overall system for generating data of a specified quality. This section provides an assessment of the QC program and a summary of resulting data quality, as determined by the QA audit.

6.1 Summary of Audit Results and Conclusions

As part of the quality assurance program for this project, a performance and systems audit was performed during the period 27 and 28 October 1981. Audit activities, results, and conclusions are presented below.

Table 6-1 is a summary of measured values for precision and accuracy of the various parameters as compared to the estimated values which were presented in the Quality Assurance Project Plan prepared for this program. Overall, the results are considered to be quite adequate to meet the program objectives in terms of data reliability. The values for measured accuracy, which are presented in Table 6-1, represent the mean value for percent accuracy with the 95 percent confidence interval for this value indicated. The values for precision represent the mean value for replicability of sample analyses. Other types of precision, which were measured (e.g., repeatability of samples, replicability of control sample analyses, etc.) are discussed and documented later in this section.

The data presented in Table 6-1, as well as the more detailed summaries presented in tables throughout this section, should be considered in terms of the data quality implications which are indicated. Looking at Table 6-1, it is seen that in most cases the measured accuracy (mean) falls well within the confidence interval defined by the precision value. An exception to this is seen for the determination of percent moisture in the atactic waste. Referring to Table 6-1, the largest (poorest) precision value measured is 14.9 percent, representing one standard deviation. If random error is considered to be the sole source of inaccuracy, then all measurements should be accurate within ± 29.8 percent of the mean (± 2 standard deviations) more than 95 percent of the time. Since the measured accuracies for both audit samples were far outside these bounds, systematic error is indicated as the source of bias. Since the moisture content of the audit samples is of the same approximate magnitude as that of the samples, the audit data should realistically reflect the quality of the sample data. Judging from the low concentrations indicated, these data indicate that the moisture contents considered were at or below the detection limit of the method. The data for the Method 25 determinations likewise tend to indicate that some inherent procedural problem is responsible for the poor precision and accuracy observed.

TABLE 6-1. SUMMARY OF ESTIMATED VERSUS MEASURED DATA QUALITY

Parameter	Accuracy		Precision	
	Estimated	Measured ¹	Estimated	Measured ²
<u>Hydrocarbon Determinations</u>				
Method 18 (on-site)	± 15%	0.21 ± 2.71%	10%	
Σ C ₂ -C ₆ (ppm level)				16.97%
Σ C ₂ -C ₆ (% level)				1.20%
Method 18 (off-site)		-5.68 ± 14.6%		1.04%
Method 25	± 10%	81.4 ± 138%	10%	22.34%/2.32% ³
Byron Method	± 10%		10%	
THC		-2.9 ± 16%		18.4%
NMHC		-4.2 ± 9.9%		23.2%
CO		12.4%		5.42%
Condensate TOC	± 20%	1.11 ± 7.92	10%	3.8%
<u>Atactic Waste Characterization</u>				
Proximate	± 10%	See Table	10%	
Ultimate	± 10%	See Table	10%	
Btu	± 10%	-2.70%	10%	0.16%
Moisture (Karl-Fischer)	± 20%	-92.1 ± 33.0%	10%	11.2%
<u>Velocity & Volumetric Flowrate</u>				
Fixed Gas Analyses	± 25%		10%	
CO ₂		-2.4 ± 8.9%		0.67%
N ₂		3.0 ± 11.4%		0.30%
O ₂		8.8 ± 82.6%		1.58%
<u>NO_x Determinations</u>	± 20%	8.97 ± 29.06%	10%	8.13%

¹Mean value plus 95% confidence interval.²Pooled relative standard deviation for replicability of sample analyses.³Tank/Trap replicability.⁴Based on systems audit results.

For both the Method 18 and Byron data, a disparity between precision (replicability) for sample analyses and that for audit sample analyses is generally apparent. This is likely due to the general inclination for variability to increase with decreasing analyte concentration. In most cases, the samples had hydrocarbon concentrations very near the detection limits of the methods. At this analyte level, however, the ultimate impact of this variability on overall data quality, i.e., calculated destruction efficiency of the incinerator, is relatively insignificant. These examples illustrate the importance of considering data quality measurements in context and using them as a tool to define the limitations of the data. From this standpoint, both the performance audit results and the systems audit conclusions indicate that the overall data quality is adequate to meet the program objectives.

6.2 Systems Audit - Approach and Conclusions

A systems audit is an on-site qualitative review of various aspects of a total sampling and/or analytical system to assess its overall effectiveness. The systems audit results represent a subjective evaluation of a set of interactive systems with respect to strengths, weaknesses, and potential problem areas. The audit was designed to evaluate the following:

- adherence to accepted procedures in performing reference method source sampling;
- adequacy of internal quality control procedures;
- equipment and facilities;
- qualification and training of personnel;
- calibration procedures and documentation;

- sample handling, custody, and storage; and
- data recording, review and handling.

The systems audit checklists, which are presented in Appendix G, delineate the specific aspects of the sampling/analytical system which are deemed to be especially important in obtaining quality data. The activities which were observed during the audit included:

- hydrocarbon determination (EPA Method 25, EPA Method 18 and the Byron Method),
- NO_x determination (EPA Method 7),
- velocity and volumetric gas flow rate determination (EPA Methods 1 and 2),
- gas phase molecular weight determination (gas partitioner), and
- collection of atactic waste samples.

As indicated on the audit checklists, careful compliance with accepted sampling procedures was observed for all sampling activities. The sampling crew exhibited an obvious familiarity with the equipment and methods used. Internal QC checks such as pre- and post-test leak checks, check of sampling train configuration, etc., were carefully followed. The facilities and procedures used in sample handling and storage were judged to be quite adequate. All data records were well organized and utilized preformatted data sheets in most instances. All equipment calibration data were complete and similarly well organized. This data is presented in Appendix G. Overall, the systems audit indicated an efficient, well orchestrated sampling effort which was judged to be adequate for achieving data quality commensurate with the program requirements.

6.3 Performance Audit

A performance audit is a quantitative assessment of the data quality of a sampling and/or analytical system. Both field and laboratory (analytical) operations were addressed in the performance audit for this program. Audit activities included:

- field check of the laboratory balances (Mettler PC 4400 and OHAUS 1119);
- checks of field calculations;
- analyses of audit gases (both on-site and off-site);
- analyses of NO_x EPA audit materials;
- blind analysis of a commercial coal standard with the atactic waste samples for proximate, ultimate and Btu analyses;
- analyses of potassium acid phthalate audit standards for TOC determination; and
- analyses of water in xylene audit standards for moisture determination using the Karl-Fischer method.

Table 6-2 lists the audit standards which were used for the performance audits.

TABLE 6-2. AUDIT STANDARDS

Parameter	Audit Material	Audit ID	Concentration	Audit Material Source
Hydrocarbon EPA Method 25	Gas Mixture	AAL 6956 ¹	CO - 56.2 ppm	Scott Environmental Technology
			CH ₄ - 52.1 ppm	"
			CO ₂ - 1.88%	"
			C ₃ H ₈ - 9.97%	"
		BAL 339	Propylene/N ₂ - 9163 ppm	US EPA
EPA Method 18	Gas Mixture	BAL 317	Propane/N ₂ - 296.0 ppm	US EPA
		AAL 6480 ¹	CO - 493 ppm	Scott Environmental Technology
			CH ₄ - 493 ppm	"
			CO ₂ - 9.97%	"
			C ₃ H ₈ - 197 ppm	"
		BAL 318	Propane/N ₂ - 19.7 ppm	US EPA
		BAL 339	(see above)	"
		BAL 317	(see above)	"
		AAL 6956	(see above)	Scott Environmental Technology
		AAL 772	CO - 0.952%	"
			CH ₄ - 1.03%	"
			CO ₂ - 12.0%	"
			O ₂ - 17.2%	"
		A 9541	CO ₂ - 46.0%	Scott Environmental Technology
			CH ₄ - 39.9%	"
			N ₂ - 9.96%	"
			O ₂ - 4.04%	"
TOC	Aqueous Potassium Acid phthalate	RAD-1	1426 ppm C	Radian
			60.5 ppm C	"
		RAD-2		
Byron Method	Gas Mixture	AAL 6480	(see above)	Scott Environmental Technology
		BAL 318	(see above)	US EPA
		AAL 772	(see above)	Scott Environmental Technology
		BAL 317	(see above)	US EPA
NO _x		SSC-1	697.3 mg/DSCM ²	US EPA
		SSC-3	298.7 mg/DSCM ²	"
		SSC-7	896.5 mg/DSCM ²	"
		SSC-8	149.4 mg/DSCM ²	"
		SSC-9	498.0 mg/DSCM ²	"
Proximate, Ultimate and BTU	Coal Standard	AR 776	11.01% Ash	Alpha Resources, Inc.
			52.45% Volatile Matter	"
			36.54% Fixed Carbon	"
			14512 BTU	"
			1.29% Sulfur	"
			76.75% Carbon	"
			6.89% Hydrogen	"
			1.30% Nitrogen	"
			0.07% Chlorine	"
H ₂ O Determination- Karl-Fischer Method	Water in Dry Xylene	RAD-1	1.14% weight H ₂ O	Radian
			0.57% weight H ₂ O	"
		RAD-2		

¹Balance Gas HC Free Air²Dry Standard Cubic Meters

6.3.1 Methods for Quantitation of Accuracy and Precision

Performance audit results presented in the following tables are expressed in terms of relative accuracy. The relative accuracy for each parameter is calculated as:

$$\% A = \frac{(M-T)}{T} \times 100$$

where,

% A = relative accuracy, percent

M = measured value

T = true value of reference standard

100 = factor for conversion to percentage basis.

The overall estimate of accuracy based upon more than one audit sample for a given analytical parameter represents the mean of the values for percent accuracy for the set of audit samples. If the associated confidence interval indicates an accuracy range which includes 0 percent, then bias cannot be confirmed based on the available data. If 0 percent is not within the indicated accuracy range, then bias, either low (-) or high (+) is indicated. The \pm value associated with the mean %A represents the 95 percent confidence interval based upon the variability of the individual %A values. The 95 percent confidence interval is calculated using a two-tailed t-test where range for %A (\pm) equals

$$t \times \frac{SD}{\sqrt{n}}$$

where,

SD = standard deviation of measured %A values based
on two or more audit samples

n = number of measured values for %A (i.e., number of audit samples)

t = t-statistic from table of t-values for Student's t-test.

When fewer than four audit standards were analyzed, the 95 percent confidence interval for the overall accuracy of the measurement becomes quite large due to the uncertainty associated with relatively few data points. This influence is seen by referring to the table of t-values below for the 95 percent confidence level using a two-tailed test.

n	df	t
2	1	12.7
3	2	4.30
4	3	3.18
5	4	2.78
6	5	2.57
7	6	2.45
8	7	2.36

n = number of measurements

df = degrees of freedom, n-1

Based on various internal QC procedures incorporated into the sampling and analytical protocol, several different aspects of sampling and/or analytical precision may be estimated from the data. One measure of analytical precision is replicability. Data used for calculating analytical replicability included results of:

- replicate analyses of process samples,
- replicate analyses of audit materials, and
- replicate analyses of control standards.

In each case, the mean (\bar{X}) and standard deviation (SD) of the values associated with a group of replicates were calculated for a given method. The overall replicability of the method, the pooled relative standard deviation (PRSD), was then calculated using the following equation:

$$\text{PRSD} = \sqrt{\frac{\sum_{i=1}^n X_i^2 DF_i}{\sum_{i=1}^n DF_i}}$$

where,

X_i = RSD of data set i ,

DF_i = degrees of freedom for data set i ($k_i - 1$).

n = total number of data sets,

k_i = number of data points in set i ,

i = data set 1, 2, 3 ... n

In instances when only two determinations were performed, i.e., duplicate analyses, the standard deviation was estimated from the relative range (percent difference) of the measurements according to the procedure outlined in Appendix C of EPA publication 600/9-76-005 (8). The RSD is calculated as:

$$\text{RSD} = \frac{\%D}{(2)^{1/2}}$$

where,

$$\%D = \frac{|X_1 - X_2|}{(X_1 + X_2)/2} \times 100$$

and,

X_1 = measurement No. 1

X_2 = measurement No. 2

A second measure of analytical precision is repeatability. This is a measure of the day-to-day variability associated with an analytical system. Generally, repeatability is estimated from repeat analyses of control standards. Repeatability is expressed as relative standard deviation, where,

$$\frac{SD}{\bar{X}} \times 100 = RSD$$

Appendix G contains control charts for the hydrocarbon (Method 18 and Byron Method) and fixed gas control samples analyses which graphically illustrate repeatability.

The concept of repeatability may be expanded to include both sampling and analytical repeatability. Sampling repeatability for this program is a measure of the variability associated with data for a given parameter (hydrocarbon and fixed gas concentrations) obtained from analyses of samples taken under the same process conditions (e.g., incinerator temperature, fuel) but at different times. This is actually a measure of total variability arising from three sources:

- analytical variability,
- sampling variability, and
- process operating variability.

The value for "sample repeatability" should generally be greater (i.e., the precision is poorer) than that for either analytical replicability or analytical repeatability since these are components of sample repeatability.

Another type of precision, which was measured for the NO_x data, is sample replicability. Here the relative standard deviation of the values for triplicate samples was calculated. This is similar to the concept of sample repeatability, but does not include the temporal variability of the process as one of the contributing components. Since all three samples of a given group were obtained at virtually the same time, only the inherent variability of the sampling method and the analytical system contribute to sample replicability. As for the analytical replicability, the RSD for each set of triplicate samples was calculated, then the pooled RSD (PRSD) was taken to represent the overall precision.

The final type of precision considered was reproducibility. This is a measure of method to method (or interlaboratory) variability for a given parameter. Reproducibility is reported only for the detailed hydrocarbon speciation analyses and is calculated using data for the audit sample analyses on the capillary column vs. the micropacked column.

The following is a brief list of general procedures used in evaluating the QA and QC data:

- mean values of replicate analyses were used in calculating the RSD for repeatability;
- mean values of replicate analyses were used in calculating relative accuracy for each parameter;
- suspect data were tested as outliers using the Dixon criteria and rejected at the 95 percent confidence level; outliers identified were not included in precision and accuracy estimates;
- values reported as "less than detection limit" were not included in precision and accuracy estimates;

- estimates of overall sample replicability, overall analytical replicability and overall sample repeatability represent the pooled relative standard deviation (PRDS); and
- the 95 percent confidence interval for the accuracy estimates were calculated from individual measurements of percent A, where the mean value for analysis of a given audit standard was used to calculate one value for percent A. When only one audit sample was analyzed, no confidence interval could be calculated.

6.3.2 Quantitation of Data Quality

The basis for the quantitation of data quality, in terms of precision and accuracy, for each measurement parameter are briefly discussed below and results are summarized in the accompanying tables.

Hydrocarbon Determinations

Hydrocarbon concentrations of the waste gas, boiler outlet gas, and natural gas were determined by three different sampling/analytical methods including proposed EPA Method 18, EPA Method 25 and the Byron Method. The data quality for these methods is summarized below.

Gas samples collected using the Method 18 integrated bag sample technique were analyzed both on- and off-site. Two Antek 460 gas chromatographs with FID detectors were used for the on-site analyses. One instrument was calibrated for carbon concentrations in the ppm range while the other was calibrated in the percent range. Appropriate level standard gas mixtures were used as control samples. Likewise, several different audit gas mixtures, in both ranges, were used to conduct the performance audits of this method. Precision and accuracy data for the Method 18 determinations are presented in Tables 6-3 and 6-4. The indicated poorer precision for

TABLE 6-3. SUMMARY OF PRECISION OF HYDROCARBON DETERMINATIONS

Method/Parameter	Samples						Control (QC) Standards						Audit Samples		
	Repeatability of Analyses			Replicability of Analyses			Repeatability of Analyses			Replicability of Analyses			Replicability of Analyses		
	\bar{X}	n ²	PRSD ³	\bar{X}	n ²	PRSD ³	\bar{X}	n ¹	RSD	\bar{X}	n ²	PRSD ³	Range ⁴	n ²	PRSD
<u>Method 18 (GC A)</u>															
CH ₄	--	--	--	--	--	--	14.7 ppmC	7	4.92%	16.0 ppmC	1	10.99%	48-44 ppm	3	1.41%
C ₂	--	--	--	--	--	--	28.2 ppmC	7	4.68%	29.4 ppmC	1	6.27%	-----	--	--
C ₃	--	--	--	--	--	--	47.1 ppmC	7	8.77%	50.7 ppmC	1	4.89%	29-893 ppm	6	0.77%
C ₄	--	--	--	--	--	--	53.0 ppmC	7	4.74%	55.4 ppmC	1	2.60%	-----	--	--
C ₅	--	--	--	--	--	--	67.4 ppmC	7	11.28%	66.9 ppmC	1	3.07%	-----	--	--
C ₆	--	--	--	--	--	--	81.1 ppmC	7	9.69%	90.7 ppmC	1	3.62%	-----	--	--
Overall (Σ C ₂ -C ₆)	2.0 ppmC	4	100.5%	2.7 ppmC	3	16.97%	55.4 ppmC	5	7.83% ⁵	58.6 ppmC	5	4.09%	29-893 ppm	6	0.77%
<u>Method 18 (GC B)</u>															
CH ₄	--	--	--	9.5% C	3	1.93	38.6 % C	4	7.58%	37.2 % C	3	3.68%	0.96-37.4%	2	3.28%
C ₂	--	--	--	--	--	--	10.1 % C	4	6.66%	9.8 % C	3	3.94%	59.7%	1	1.54%
C ₃	--	--	--	--	--	--	6.3 % C	4	6.49%	6.1 % C	3	4.09%	31.6%	1	1.12%
C ₄	--	--	--	--	--	--	4.1 % C	4	4.25%	4.0 % C	3	7.71%	-----	--	--
C ₅	--	--	--	--	--	--	4.7 % C	4	7.38%	4.7 % C	3	15.4%	-----	--	--
C ₆	--	--	--	--	--	--	1.3 % C	4	9.37%	1.3 % C	3	21.1%	-----	--	--
Overall (Σ C ₂ -C ₆)	9.7% C	5	26.08%	9.9% C	6	1.20	5.3 % C	5	6.83% ⁵	5.2 % C	15	10.44%	31.6-59.7%	2	1.33%

¹Number of sets of repeat samples or standards.²Number of sets of replicate samples or standards.³Pooled relative standard deviation for all sets of replicates or repeats.⁴Range of concentrations of audit gas mixtures for each component.⁵Pooled RSD for C₂-C₆.

(Continued)

TABLE 6-3 (Continued).

Method/Parameter	Samples						Control (QC) Standards						Audit Samples		
	Repeatability of Analyses			Replicability of Analyses			Repeatability of Analyses			Replicability of Analyses			Replicability of Analyses		
	\bar{X}	n ¹	PRSD ³	\bar{X}	n ²	PRSD ³	\bar{X}	n ¹	RSD	\bar{X}	n ²	PRSD ³	Range ⁴	n ²	PRSD ³
<u>Byron Method</u>															
THC	1.7 ppmC	6	40.42%	1.7 ppmC	13	18.4%	648 ppmC	3	1.44 %	648 ppmC	3	0.58%	28.7 ppmC- 1.17% C	5	0.49%
NMHC	1.0 ppmC	5	38.89%	1.0 ppmC	11	23.2%	621 ppmC	3	4.00 %	621 ppmC	3	1.21%	26.1-836 ppmC	5	1.44%
CO	1.8 ppmC	2	44.46%	2.7 ppmC	8	5.42%	528 ppmC	3	0.808%	528 ppmC	3	0.80%	1.07% C	1	1.43%
Overall	1.4 ppmC	13	40.2%	1.7 ppmC	32	18.2%	599 ppmC	9	2.1%	599 ppmC	9	0.86%	26 ppmC- 1.17% C	11	1.10%
<u>Method 25</u>															
Light HC (Tank)	27.0 ppmC	4	39.74%	29.8 ppmC	12	22.34%	-----	--	-----	-----	--	-----	208 ppmC	5	5.44%
Heavy HC (Trap)	303 ppmC	7	76.55%	418 ppmC	17	2.86%	-----	--	-----	-----	--	-----	94 ppmC	2	3.75%
Total HC	319 ppmC	7	74.89%	-----	--	-----	-----	--	-----	-----	--	-----	-----	--	-----

¹Number of sets of repeat samples or standards.²Number of sets of replicate samples or standards.³Pooled relative standard deviation for all sets of replicates or repeats.⁴Range of concentrations of audit gas mixtures for each component.⁵Pooled RSD for C₂-C₆.

TABLE 6-4. SUMMARY OF PERFORMANCE AUDIT RESULTS FOR METHOD 18 ON-SITE HYDROCARBON DETERMINATIONS

Sample Identification	GC ID	C ₁				C ₂				C ₃			
		Measured Conc.		Actual Conc. ³	XA	Measured Conc.		Actual Conc. ³	XA	Measured Conc.		Actual Conc. ³	XA
		Mean ¹	RSD ²			Mean ¹	RSD ²			Mean ¹	RSD ²		
ARCO-060 (Cyl #AAL-6480)	A	440 ppm ⁴	1.13%	493	-10.75					572 ppm ⁴	0.12%	591 ppm	- 3.2
ARCO-061 (Cyl #BAL-318)	A									59.6 ppm	0.59%	59.1 ppm	0.84
ARCO-065 (Cyl #BAL-339)	A									28.8 ppm	0.98%	28.9 ppm	- 0.35
ARCO-069 (Cyl #BAL-317)	A									892 ppm ⁴	1.82%	888 ppm	0.45
ARCO-074 (Cyl #AAL-6956)	A	47.5 ppm	1.19%	52.1 ppm	- 8.83					57.8 ppm	0.73%	59.4 ppm	- 2.69
ARCO-096 (Cyl #AAL 6956)	A	47.8 ppm	1.92%	52.1 ppm	- 8.25					58.2 ppm	0.36%	59.4 ppm	- 2.02
ARCO-12A (Cyl #A-9451)	B	37.4%	3.03%	39.98%	- 6.45								
ARCO-13A (Cyl #A-5401)	B					59.6%	1.54%	59.8 %	- 0.33	31.6%	1.12%	29.97 %	5.44
Mean XA = - 8.57 ± 2.82						Mean XA = - 0.33				Mean XA = - 0.21 ± 2.71			

¹Mean value of duplicate analyses, ppmv-C (GC A) or % C, v/v (GC B).²Relative standard deviation of duplicate analyses, %.³Certified concentration of audit gases, ppmv-C or % C, v/v.⁴Measured value was outside instrument calibration and working ranges.

replicability of sample analyses, as compared to replicability for control samples or audit samples, is most likely a function of the low hydrocarbon concentrations encountered.

Four gas samples obtained at the boiler outlet of the incinerator were shipped in sample canisters to Radian's Austin laboratory for detailed gas chromatographic speciation. The analyses were performed on a Varian 3700 gas chromatograph. Two audit samples were introduced into similar canisters and shipped for analysis along with the actual samples. The audit results for these samples is presented in Table 6-5. Precision data for the off-site GC analyses is presented in Table 6-6.

The EPA Method 25 determinations of the total gaseous non-methane organic emissions from the flue gas were performed by Pollution Control Science, Inc. (PCS). A total of 19 samples were collected at the waste heat boiler outlet and analyzed off-site. Five audit samples were provided to PCS by Radian's quality assurance personnel. Of these five samples, one pair of samples was taken from each of two different audit gas mixtures. For each pair, one sample was collected using the sample train configuration used for actual samples, with the water knockout in place. The other sample of the pair was collected with the water knockout omitted. The fifth sample represents a third mixture collected using the moisture knockout. Based on the measured accuracies for these analyses, data pertaining to errors associated with use of the moisture knockout are inconclusive, as shown in Table 6-7. Precision data for the method are summarized in Table 6-3.

The third method for VOC determinations used was the Byron Method. The results of these analyses generally agreed with those obtained by Method 18. Measured values for precision and accuracy are also generally comparable, as indicated in Tables 6-3 and 6-8.

For all three of the above methods, the performance audit consisted of submitting certified standard gas mixtures for analysis along with actual

TABLE 6-5. PERFORMANCE AUDIT RESULTS FOR OFF-SITE METHOD 18 HYDROCARBON SPECIATION

Sample Identification	CAPILLARY COLUMN					MICROPACKED COLUMN				
	Measured \bar{X}^1	n^2	RSD ³	Actual	%A	Measured \bar{X}^1	n^2	RSD ³	Actual	%A
ARCO 104 (Cyl #BAL 339)	25.48 ⁴	3	2.16	28.9	-11.8	27.70 ⁴	3	0.26	28.9	-4.2
ARCO 105 (Cyl #AAL 6956)	51.46 ⁵	3	1.09	59.4	<u>-13.4</u>	63.39 ⁵	3	0.67	59.4	<u>6.7</u>
					Mean % A = -12.6±10.2%					

¹Mean of replicate analyses, ppmv-C.²Number of replicates.³Relative standard deviation of replicates, percent.⁴Qualitatively identified as propylene.⁵Qualitatively identified as propane.

TABLE 6-6. SUMMARY OF PRECISION¹ FOR OFF-SITE METHOD 18 HYDROCARBON SPECIATION

Column/Sample ID	<u>REPLICABILITY OF ANALYSES</u>			<u>REPRODUCIBILITY² OF ANALYSES</u>		
	\bar{X} (ppmv-C)	n	RSD	\bar{X} (ppmv-C)	n	RSD
<u>Capillary Column</u>						
ARCO 104 (Cyl #BAL 339)	25.48	3	2.16%	26.59	2	5.90%
ARCO 105 (Cyl #AAL 6956)	51.46	3	1.09%	57.42	2	14.69%
			PRSD = 1.58%			PRSD = 10.30%
<u>Micropacked Column</u>						
ARCO 104 (Cyl #BAL 339)	27.70	3	0.26%			
ARCO 105 (Cyl #AAL 6956)	63.39	3	0.67%			
			PRSD = 0.46%			

¹Based on analyses of audit samples only.

²Results for capillary column versus micropacked column.

TABLE 6-7. SUMMARY OF EPA METHOD 25 PERFORMANCE AUDIT RESULTS

Sample Identification	Measured Concentration (ppm-C)				Total ³	Actual Concentration ⁴	% A
	Tank		Trap				
	Mean ¹	RSD ²	Mean ¹	RSD ²			
ARCO-109 ⁵ (Cyl #AAL-6956)	75.2	5.4%	151	1.66%	217	59.4	265 %
ARCO-110 ⁶ (Cyl #ALL-6956)	88.2	4.5%	< 15	----	88.2	59.4	48.5%
ARCO-113 ⁶ (Cyl #BAL-339)	28.7	7.6%	37.2	5.81%	57.2	28.89	98.0%
ARCO-114 ⁵ (Cyl #BAL-339)	30.4	7.2%	< 15	----	30.4	28.89	3.6%
ARCO-121 ⁶ (Cyl #BAL-317)	815	2.5%	< 15	----	815	888	- 8.2%
							81.4 ± 138

¹Mean concentration of replicate analyses.

²Relative standard deviation for replicate analyses.

³Total reported concentration, ppmv-C, total non-methane hydrocarbon.

⁴Certified concentration of audit gas, ppmv-C, total non-methane hydrocarbon.

⁵Moisture knockout omitted from sample train for audit gas sample.

⁶Audit sample introduced through complete sampling train with moisture knockout as used for sample collection.

89

¹Mean value of replicate analyses, ppmv-C except as noted.

²Relative standard deviation of replicate analyses.³Hydrocarbon residue - not quantified.

samples. Three of these audit gas mixtures were obtained from the Quality Assurance Management Staff of the U.S. Environmental Protection Agency (EPA). The audit samples for the Byron method and the on-site Method 18 determinations were introduced into clean Tedlar bags by the auditor and given to the scientists performing the analyses as blind samples. Samples for off-site analysis were introduced into collection vessels identical to those for actual samples. Precision estimates for the methods are based upon results of replicate analyses of samples, control standards, and audit samples, repeat samples obtained under similar process conditions, and repeat analyses of control standards.

Samples of aqueous condensate collected in the moisture knockouts were submitted for TOC analysis to determine the contribution of emissions if this is defined as VOC. The data quality of these analyses are summarized in Tables 6-9 and 6-10. Aqueous solutions of potassium acid phthalate were prepared by personnel not associated with the sample analyses. Different batches, at different concentrations, were used as control standards and audit samples.

Atactic Waste Characterization

In order to assess the atactic waste, in terms of characteristics related to its use as a fuel, 17 samples were submitted for proximate, ultimate, and Btu analysis. Eight samples were also submitted for moisture determinations by the Karl-Fisher titration method. Commercial Testing and Engineering Company (CT&E) was subcontracted to perform these analyses. Three blind duplicates were submitted for the proximate, ultimate, and Btu analyses, and two were submitted for moisture determination. A certified coal sample was used as the audit sample for the former, while two samples of water in dry xylene were used for the latter. Precision and accuracy data for the ultimate/proximate analyses are summarized in Table 6-11 and 6-12. These data for the moisture determinations are presented in Tables 6-13 and 6-14. Considering the accuracy data for the moisture determinations,

TABLE 6-9. SUMMARY OF PRECISION OF TOC ANALYSES

Sample ID	Replicability of Sample Analyses			Repeatability of QC Sample Analyses		
	\bar{X}^1	n^2	RSD ³	\bar{X}^1	n^2	RSD ³
ARCO 084	47	2	6.0			
ARCO 057	0	2	0.0			
ARCO 123	775	2	8.2			
ARCO 002-80	835	2	0.8			
TOC Control				32	3	4.8
Overall		PRSD = 3.8				

¹Mean of replicate analyses, ppm-C

²Number of replicates.

³Relative standard deviation of replicate analyses, percent.

⁴Pooled RSD for all samples.

TABLE 6-10. SUMMARY OF PERFORMANCE AUDIT DATA FOR TOC ANALYSES

Sample ID	Measured Conc.	Actual Conc.	%A ¹
Audit #1	1346	1426	-5.61
Audit #1	1385	1426	-2.88
Audit #2	605	605	0.00
Audit #2	624	605	3.14
Audit #2	671	605	10.91
Overall % A =			1.11±7.92%

¹Based on single daily determinations of the two audit standard solutions.

TABLE 6-11. SUMMARY OF ANALYTICAL PRECISION OF PROXIMATE AND ULTIMATE ANALYSES

Parameter	Sample No. 055			Sample No. 077			Sample No. 079			Analytical Replicability	
	\bar{X}^1	n ²	RSD ³	\bar{X}^1	n ²	RSD ³	\bar{X}^1	n ²	RSD ³	PSRD (%) ⁴	n
<u>Proximate</u>											
% Moisture	0.10	2	7.4	0.19	2	14.9	-----	---	-----	11.2	3
% Ash	0.72	2	0.98	0.72	2	2.93	0.55	2	33.4	12.4	3
% Volatile	99.28	2	0.01	99.28	2	0.02	0.45	2	0.18	0.07	3
% Fixed Carbon	0.0	2	0.0	0.0	2	0.0	0.0	2	0.0	0.0	3
Btu/lb	18520	2	0.02	18635	2	0.12	18540	2	0.33	0.16	3
% Sulfur	0.22	2	47.1	0.24	2	51.2	0.28	2	7.71	35.3	3
<u>Ultimate</u>											
% Carbon	75.91	2	0.26	75.90	2	0.21	75.59	2	0.24	0.24	3
% Hydrogen	12.92	2	0.16	12.92	2	0.66	13.01	2	0.87	0.56	3
% Nitrogen	0.14	2	10.1	0.15	2	0.0	0.19	2	14.9	8.30	3
% Chlorine	0.56	2	3.75	0.54	2	16.9	0.56	2	6.37	9.01	3
% Sulfur	0.22	2	47.1	0.24	2	51.2	0.28	2	7.71	35.3	3
% Ash	0.72	2	0.98	0.72	2	2.93	0.55	2	33.4	12.4	3

¹Mean value for replicate analyses.²Number of replicates.³Relative standard deviation of replicates.⁴Pooled relative standard deviation.

TABLE 6-12. SUMMARY OF PERFORMANCE AUDIT RESULTS FOR
PROXIMATE AND ULTIMATE ANALYSES

PARAMETER	MEASURED*	ACTUAL*	RELATIVE ACCURACY
<u>Proximate</u>			
% Moisture	0.40	-	-
% Ash	9.52	11.01	-13.5
% Volatile	52.69	52.45	0.46
% Fixed Carbon	37.79	36.54	3.42
Btu/lb.	14120	14512	-2.70
% Sulfur	1.39	1.29	7.75
<u>Ultimate</u>			
% Carbon	78.86	76.75	-3.77
% Hydrogen	5.86	6.89	-14.9
% Nitrogen	1.25	1.30	-3.85
% Chlorine	0.13	0.07	85.7
% Sulfur	1.39	1.29	7.75
% Ash	9.52	11.01	-13.5

*All values except moisture on a dry basis; measured values based on a single determination.

TABLE 6-13. SUMMARY OF ANALYTICAL REPLICABILITY OF WATER DETERMINATION

<u>Replicability of Sample Analyses</u>			
Sample ID	\bar{X}^1	n^2	RSD ³
#055-A/B	0.10%	2	7.4
#077-A/B	0.19%	2	14.9
PRSD = 11.2			

¹Mean value of replicate analyses.

²Number of replicates.

³Relative standard deviation of mean, percent.

TABLE 6-14. SUMMARY OF PERFORMANCE AUDIT RESULTS FOR
KARL-FISCHER MOISTURE DETERMINATIONS

Sample ID	Measured* (% Weight)	Actual (% Weight)	Relative Accuracy
RAD-1	0.06	1.14	-94.7
RAD-2	0.06	0.57	-89.5
Mean % A = -92.1±33.0			

*Measured value represents mean of replicate analyses.

it appears that both the samples and the audit standards had water concentrations at or below the detection limit of the method, resulting in the rather poor analytical accuracy.

Velocity and Volumetric Flowrate

The U.S. EPA has conducted extensive collaborative testing to define the achievable accuracy and precision of the Reference Method test procedures for source sampling. Independent evaluation and measurement of precision and accuracy of procedures such as the determination of velocity and volumetric flowrate relies upon the results of these tests and systems audit results, i.e., subjective appraisal of the techniques used. The systems audit results are augmented by performance audits of component parts of the procedure when direct measure of data quality is possible. Results of the on-site fixed gas analyses were used to calculate gas molecular weight (modified Method 3) which, in turn, is used in calculating velocity and volumetric flowrate. As for the hydrocarbon analyses, standard gas mixtures were submitted for analysis to facilitate a performance audit of this procedure. Results are summarized in Table 6-15. Precision data for the fixed gas analyses is presented in Table 6-16. Based upon these data and the systems audit results, the velocity and volumetric flowrate determinations should be within the precision and accuracy ranges estimated for the methods.

NO_x Determinations

Five sets of triplicate NO_x samples were collected during the field sampling effort. Analyses of these samples were performed at Radian's Austin laboratory. When the samples were analyzed initially, three samples were split and analyzed as duplicates. The precision (analytical replicability) of these analyses was not as good as that typically associated with this method. The accuracy of the analyses, as measured by results for EPA NO_x audit materials (two samples) also indicated the possibility of problems, although no bias was indicated since the measured NO_x concentrations were

TABLE 6-15. SUMMARY OF PERFORMANCE AUDIT RESULTS FOR FIXED GAS ANALYSES

Sample Identification	CH ₄			CO ₂			CO			O ₂			N ₂		
	Measured Conc. ¹	Actual Conc. ²	%A	Measured Conc. ¹	Actual Conc. ²	%A	Measured Conc. ¹	Actual Conc. ²	%A	Measured Conc. ¹	Actual Conc. ²	%A	Measured Conc. ¹	Actual Conc. ²	%A
ARCO-060 (Cyl #AAL-6480)	N/A ³	----	----	9.66	9.97	- 3.1	----	----	----	21.8	18.9	15.3 ⁴	71.8	70.3 ⁴	2.1
ARCO-062 (Cyl #AAL-772)	1.04	1.03	0.97	11.8	12.0	- 1.7	1.16	0.952	21.8	17.6	17.2	2.3	72.7	68.8 ⁴	3.9
	Mean %A = 0.97			Mean %A = 2.4 ± 8.9			Mean %A = 21.8			Mean %A = 8.8 ± 82.6			Mean %A = 3.0 ± 11.4		

¹Mean value for duplicate analyses, percent by volume.²Certified concentration of audit gas, percent by volume, except as noted.³Not analyzed.⁴Calculated concentration based on balance gas used, air or nitrogen.

TABLE 6-16. SUMMARY OF PRECISION FOR FIXED GAS DETERMINATIONS

Parameter	Samples						Control (QC) Standards						Audit Samples		
	Repeatability of Analyses			Replicability of Analyses			Repeatability of Analyses			Replicability of Analyses			Replicability of Analyses		
	\bar{X}	n ¹	PRSD ³	\bar{X}	n ²	PRSD ³	\bar{X}	n ¹	RSD	\bar{X}	n ²	PRSD ³	Range ⁴	n ²	PRSD ³
CO ₂	5.2%	8	6.27%	5.2%	17	0.67%	19.6%	8	0.84%	19.5%	4	0.67%	10.7%	2	0.75%
N ₂	87.7%	12	0.57%	86.4%	19	0.30%	65.2%	8	4.96%	62.9%	2	0.38%	72.2%	2	0.46%
O ₂	9.1%	13	50.96%	11.4%	21	1.58%	15.2%	8	1.18%	15.1%	4	0.43%	19.7%	2	0.77%
CO	---	--	---	---	--	---	1.1%	8	4.69%	1.15%	4	1.50%	---	--	---
CH ₄	---	--	---	---	--	---	1.0%	8	6.06%	1.03%	4	3.13%	---	--	---

¹Number of sets of repeat samples or standards.

²Number of sets of replicate samples or standards.

³Pooled relative standard deviation for all sets of replicates or repeats.

⁴Range of concentrations of audit gas mixtures for each component

within the range predicted by the measured precision. To check the initial analyses, approximately one-half of the samples were reanalyzed on two subsequent days. The results for these repeat analyses were ultimately invalidated based on the results for the audit samples analyzed concurrently. These repeat data are not included in the summaries of precision and accuracy. A second set of repeat analyses were performed approximately two months after the original analyses by a different analyst using different equipment and reagents. These results compared favorably with the original values for the seven samples which were repeated. Table 6-17 summarizes the precision data for the NO_x determinations with respect to replicability and repeatability. The results of the audit sample analyses are summarized in Table 6-18. Results for the two samples which led to the invalidation of the first set of repeat analyses are included in this table but are not considered to be indicative of the accuracy for the reported results.

Field Check of Laboratory Balances

The accuracy of the laboratory balances, a Mettler PC 4400 and an OHAUS Model 1119, was checked using a set of NBS traceable Class S weights. Replicate weighings were made on weights ranging from 1.0 gram to 100 grams. On the Mettler PC 4400 balance, differences between balance reading and actual weight were observed for the 50 g and 100 g weights. The difference with the 50 g weight was 0.02 g or 0.04 percent; the difference with the 100 g weight was 0.01 or 0.01 percent. The OHAUS Model 1119 balance had the greatest difference using the 10.0 g weight. This difference was 0.02 or -2.0 percent.

TABLE 6-17. SUMMARY OF PRECISION FOR NO_x ANALYSES

SAMPLES								AUDIT STANDARDS							
Replicability of Samples ¹				Replicability of Analyses				Repeatability of Analyses				Replicability of Analyses			
Sample	\bar{X}^2	n ³	RSD	Sample	\bar{X}^2	n ³	RSD	Sample	\bar{X}^1	n ²	RSD	Sample	\bar{X}^1	n ²	RSD
018	63.92	2 ⁴	6.7	064-2	64.14	2	13.8	018-1	59.42	2	2.4	Audit #7	1140	2	21.7
037	76.09	3	14.4	125-1	59.64	2	2.14	037-2	43.24	2	15.2	Audit #8	147.9	2	7.03
064	68.31	3	5.8				PRSD = 8.0	037-3	76.00	2	13.3	Audit #1	688.5	2	1.95
097	112.4	3	4.2					097-1	107.9	2	11.2				PRSD = 10.2
125	57.89	3	4.0					097-2	102.7	2	6.3				
			PRSD = 8.1					125-3	55.3	2	13.1				
								064-3	66.72	2	11.2				
											PRSD = 10.4				

¹Triplicate samples taken simultaneously.² \bar{X} = mean value of n measurements, mg/DSCM³n = number of measurements.⁴One of three measurements rejected as outlier at 95% confidence level.

TABLE 6-18. SUMMARY OF NO_x AUDIT SAMPLE ANALYSES

Audit Sample Identification	Measured		Actual	%A
	Mean ¹	RSD ²		
7	1140.3	21.7	896.5	27.2
8	147.9	7.03	149.4	1.02
9	824.0	5.33	498.0	65.5 ³
3	179.8	14.4	298.7	-39.8 ³
1	688	2.0	697.3	- 1.3
Overall				8.97 ⁴ ±29.06

¹Mean value of duplicate analyses, mg/DSCM.

²Relative standard deviation of duplicate analyses.

³Results of samples analyzed along with these audit samples were invalidated. These values are not included in estimated overall accuracy.

⁴Mean value for audit samples #7, #8, and #1.

7.0 RESULTS

This section discusses the detailed results which include the following major topics:

- composition of gases,
- organics in condensate catches,
- composition of atactic waste,
- calculations, and
- miscellaneous results such as NO_x data and inorganic species in the gas from the incinerator

The results of all analyses which impact the destruction efficiencies are presented first, then the calculations for the destruction efficiencies are presented.

7.1 Gas Phase Data

The following subsections include discussions of various gas phase analytical results. Instead of presenting separate tables for each type of analysis, Table 7-1 is presented here so that all data can be viewed together. This table includes:

- sample identification numbers so that the raw data in the appendices can be matched to the data presented in the table,
- process data summary which can also be found in the appendices where all values are recorded;

TABLE 7-1. INCINERATOR DATA SUMMARY FOR EACH SAMPLING RUN

Date	10/21**	10/21**	10/22	10/22	10/22	10/26	10/26	10/26	10/26
Sample ID:									
Method 18	004	002	011	021	024	027	033	044	049
Volumetric Flow	019	019	016	026	-	035	-	041	047
Byron 401	005	009	017	023	028	034	042	045	051
Method 25	-	006	010	022	029	036	040	046	053
Time (Test Start)	1100	1310	0903	1255	1548	0840	1145	1355	1626
Sample Location (1)	80	80	80	80	80	80	80	80	80
Process Data									
Fuel Condition (1)	AW/NG	AW/NG	AW/NG	AW/NG	AW/NG	AW/NG	AW/NG	AW/NG	AW/NG
Incinerator Temp. (°F)	1800	1800	1800	1800	1800	1600	1600	1600	2000
N ₂ Flow (x1000 SCFH)	6.2	6.2	6.2	6.4	6.4	5.1	4.2	5.2	5.2
Natural Gas Flow (x3500 SCFH)	2.6	2.6	2.6	2.6	2.6	3.4	3.2	3.2	7.5
Fixed Gases									
Method 25									
CO ₂ %	5.27±.06	4.95±.05	5.48±.01	5.29±.02	5.20±0	4.80±0	4.58±.03	4.81±0	6.75±.09
CO%	0	0	0	0	0	0	0	0	0
N ₂ %	69(2)	69(2)	81.70	81.20±0	81.15±.07	82.15±.21	81.4±.71	81.55±.21	83.0±.28
O ₂ %	13.54±.16	13.45±.08	14.10±0	14.25±.07	14.50±.12	15.05±.07	15.2±.14	14.85±.07	12.05±.07
Volumetric Flow									
Time	1513	1513	1050	1417		0910		1325	1640
SO Temp (°F)	132	132	122	130		127		127	133
Bar. Pressure (°Hg)	30.5	30.5	30.4	30.4		30.5		30.5	30.5
ΔP (°H ₂ O)	.32	.32	.31	.31		.17		.16	.15
Velocity (fps)	34	34	33	33		25		24	23
ACFM	40,200	40,200	38,900	39,500		28,900		28,000	27,300
SCFM (dry)	30,100	30,100	31,000	30,000		22,400		21,700	20,400
% Moisture (3)	16	16	12	15		14		14	16
Hydrocarbons									
Method 18									
BO (ppm - C ₂ -C ₆)	259.4	649.3	153.0	3.55±.07	6.4	<1.0	1.6	<1.0	1.6
WG (vol.% - C ₂ -C ₆)									
NG (vol.% - CH ₄)									
(vol.% - C ₂ -C ₆)									
Byron 401 (ppmv-C)									
THC (w/ascarite)		41±.8		11	6±.11	1.3±.17	3.4±.48	1.9±.03	2.9±.07
THC (wo/ascarite)	169±1.65	61.6±1.9	98±.59	11	6±.15	1.1±.02	3.4(4)	1.9(4)	2.1±.31
NMHC (w/ascarite)		45±.52							1.0
NMHC (wo/ascarite)	155	86±10	123±13	59	55±.21	<0.5*	<0.5*	<0.5*	2.1(4)
CO (w/ascarite)		347±.46							2.0
CO (wo/ascarite)	17	327±.16	315±0						.7
Method 25 (5)									
NMHC		1111	2826	570	289	881	125	314	1806
Speciated HC-TMHC (ppmv-C)							0.84		

(Continued)

*For two determinations

**Shakedown run data presented for completeness only

(1) - AW = Atactic Waste, NG = Natural Gas, WG = Waste Gas, BO = Waste Heat Boiler Outlet

(2) - Data not valid since concentration was outside range of calibration standard

(3) - Determined from psychometric chart.

(4) - Difficulties with analysis. Value given represents probable concentration

(5) - Data not believed to represent true values

TABLE 7-1. (CONTINUED)

Date	10/27	10/27	10/27	10/27	10/27	10/27	10/27	10/27
Sample ID:								
Method 18	054	057	038	063	067	078	075	080
Volumetric Flow	-	071	052	-	073	082	-	-
Byron 401	058	068	-	-	072	081	-	-
Method 25	059	066	-	-	076	083	-	-
Time (Test Start)	1020	1304	1026	1302	1520	1713	1520	1713
Sample Location (1)	RO	RO	WG	WG	RO	RO	WG	WG
Process Data								
Fuel Condition (1)	AW/NG/WG	AW/NG/WG	AW/NG/WG	AW/NG/WG	AW/NG/WG	AW/NG/WG	AW/NG/WG	AW/NG/WG
Incinerator Temp (*F)	1600	1600	1600	1600	1800	1800	1800	1800
H ₂ Flow (x1000 SCFH)	6.3	6.2	6.3	6.2	6.2	6.2	6.2	6.2
Natural Gas Flow (x3500 SCFH)	4.0	4.5	4.0	4.5	5.8	5.7	5.8	5.7
Fixed Gases								
Method 1A								
CO ₂ %	4.64	4.59±.08	0	0	5.62±.01	6.73±.05	0	0
CO%	0	0	0	0	0	0	0	0
N ₂ %	82.3±.64	82.6	94.1±.57	95.55±.07	83.15±.21	82.35±.21	95.05±.07	95.7
O ₂ %	15.0±0	14.95±.07	0.68±.11	2.39	13.4±0	13.5±0	2.79	1.36
Volumetric Flow								
Time		1425	1035		1530	1730		
SO Temp. (*F)		128	128		131	133		
Bar. Pressure ("Hg)		30.5	30.5		30.5	30.5		
ΔP ("H ₂ O)		.15	.14		.15	.15		
Velocity (fps)		23	22		23	23		
ACFM		27,200	26,300		27,300	27,300		
SCFM (dry)		21,000	20,300		20,700	20,400		
% Moisture (3)		14	14		15	16		
Hydrocarbons								
Method 1B								
RO (ppm - C ₂ -C ₆)	1.13±.39	<1.0	14.4	5.53±.07	<1.0	<1.0	7.38	7.76
WG (vol.% - C ₂ -C ₆)								
NG (vol.% - C ₂ -C ₆)								
(vol.% - C ₂ -C ₆)								
Byron 401 (ppmv-C)								
TIC (w/ascarite)	1.3±.23	1.5±.11			2.1±.49	1.2±.24		
TIC (w/ascarite)								
NMHC (w/ascarite)	1.5±.25	1.6±.22			1.4±.20	0.7±02		
NMHC (w/ascarite)								
CO (w/ascarite)	6±0	6±.05			2.1±.23	3.2±.14		
Method 25 (5)								
NMHC	103	182			79.5	108		

(Continued)

*For two determinations

**Shakedown run data presented for completeness only

(1) - AW = Atactic Waste, NG = Natural Gas, WG = Waste Gas, RO = Waste Heat Boiler Outlet

(2) - Data not valid since concentration was outside range of calibration standard

(3) - Determined from psychometric chart.

(4) - Difficulties with analysis. Value given represents probable concentration

(5) - Data not believed to represent true values

TABLE 7-1. (CONTINUED)

Date	10/28	10/28	10/28	10/28	10/28	10/28	10/28	10/28
Sample ID:								
Method 18	084	090	085	091	100	103	098	108
Volumetric Flow	087	095	-	-	101	107	-	-
Byron 401	086	094	-	-	099	106	-	-
Method 25	088	093	-	-	102	111	-	-
Time (Test Start)	0927	1126	0926	1123	1422	1643	1419	1640
Sample Location (1)	BO	BO	WG	WG	BO	BO	WG	WG
Process Data								
Fuel Condition (1)	AW/NG/WG	AW/NG/WG	AW/NG/WG	AW/NG/WG	NG/WG	NG/WG	NG/WG	NG/WG
Incinerator Temp. (°F)	2000	2000	2000	2000	1800	1800	1800	1800
N ₂ Flow (x1000 SCFH)	6.1	6.0	6.1	6.1	6.1	6.1	6.1	6.1
Natural Gas Flow (x3500 SCFH)	7.7	7.6	7.7	7.6	>10	>10	>10	>10
Fixed Gases								
Method 18								
CO ₂ %	6.52±.06	6.39±.011	0	0	4.76±0	4.76	0	0
CO%	0	0	0	0	0	0	0	0
N ₂ %	83.65±.21	83.45±.07	94.3±.14	93.30	83.4±.14	83.2	94.80±0	95.55±.92
O ₂ %	11.65±.07	11.9±0	2.2±0	2.21	13.3±0	13.5	1.69±0	1.10±.01
Volumetric Flow								
Time	1000	1135			1533	1720		
SO Temp. (°F)	136	135			134	137		
Bar. Pressure ("Hg)	30.5	30.5			30.5	30.5		
ΔP ("H ₂ O)	.14	.14			.13	.12		
Velocity (fps)	22	22			22	21		
ACFM	26,400	26,400			25,400	24,500		
SCFM (dry)	19,200	19,500			19,000	17,800		
% Moisture (3)	18	17			16	18		
Hydrocarbons								
Method 18								
RO (ppm - C ₂ -C ₆)	1.63	<1.0			<1.0	<1.0		
WG (vol.% - C ₂ -C ₆)			9.88±.04	11.76±.13			8.02±.10	10.70±.28
NG (vol.% - CH ₄)								
(vol.% - C ₂ -C ₆)								
Byron 401 (ppmv-C)								
THC (w/ascarite)	3.3±.32	2.3±.97			0.7±.30	1.5±.38		
TIC (wo/ascarite)								
NMHC (w/ascarite)	0.7±.18	1.8±.87			0.3±.12	1.0±.24		
NMHC (wo/ascarite)								
CO (w/ascarite)	<0.5	3.1±.06			0.7±.01	3.9±.12		
CO (wo/ascarite)								
Method 25 (5)								
THWIC	69.4	69.7			66.8	192		

(Continued)

*For two determinations

**Shakedown run data presented for completeness only

(1) - AW = Attacked Waste, NG = Natural Gas, WG = Waste Gas, BO = Waste Heat Boiler Outlet

(2) - Data not valid since concentration was outside range of calibration standard

(3) - Determined from psychometric chart.

(4) - Difficulties with analysis. Value given represents probable concentration

(5) - Data not believed to represent true values

TABLE 7-1. (CONTINUED)

Date	10/29	10/29	10/29	10/29	10/26	10/26	10/29
Sample ID:							
Method 18	112	117	120	123	050	056	126
Volumetric Flow	116	118	-	-	-	-	-
Byron 401	115	119	-	-	-	-	-
Method 25	122	27	-	-	-	-	-
Time (Test Start)	0858	1100	0856	1100	1506	1648	1027
Sample Location (1)	BO	BO	WG	WG	NG	NG	NG
Process Data							
Fuel Condition (1)	NG/WG	NG/WG	NG/WG	NG/WG	NG/AW	NG/AW	NG/WG
Incinerator Temp. (°F)	1600	1600	1600	1600	1800	2000	1600
N ₂ Flow (x1000 SCFH)	4.0	4.0	4.0	4.0	5.2	5.2	4.0
Natural Gas Flow (x3500 SCFH)	9.3	9.3	9.3	9.3	5.5	7.4	9.3
Fixed Gases							
Method 18							
CH ₄ %	4.10±.02	4.96	0	0	.80	.80±.02	1.74
CO%	0	0	0	0	0	0	0
N ₂ %	83.3±.14	82.2	95.3	95.5	0	0	0
O ₂ %	14.75±.07	14.5	0.07	0.55	0	0	0
Volumetric Flow							
Time	0915	1120					
SO Temp. (°F)	134	133					
Bar. Pressure (°Hg)	30.5	30.5					
ΔP (°H ₂ O)	.12	.13					
Velocity (fps)	21	22					
ACFM	24,400	25,400					
SCFM (dry)	18,200	19,000					
% Moisture (3)	16	16					
Hydrocarbons							
Method 18							
BO (ppm - C ₂ -C ₆)	<1.0*	<1.0	13.25±.07	8.44			
WG (vol.% - C ₂ -C ₆)					75.9±1.3	75.6±1.7	77±1.4
NG (vol.% - CH ₄)					6.39±.23	6.63±.13	15.35±.03
(vol.% - C ₂ -C ₆)							
Byron 401 (ppmv-C)							
THC (w/ascarite)	0.6±.05	1.1±.15					
THC (wo/ascarite)							
NMHC (w/ascarite)	0.5±.22	0.47±.11					
NMHC (wo/ascarite)							
CO (w/ascarite)	1.3±.02	1.2±.23					
CO (wo/ascarite)							
Method 25 (5)							
NMHC							
Speciated HC-TMHC (ppmv-C)		0.49±.07					

*For two determinations

**Shake down run data presented for completeness only

- (1) - AW = Atactic Waste, NG = Natural Gas, WG = Waste Gas, BO = Waste Heat Boiler Outlet
 (2) - Data not valid since concentration was outside range of calibration standard
 (3) - Determined from psychometric chart.
 (4) - Difficulties with analysis. Value given represents probable concentration
 (5) - Data not believed to represent true values

- volumetric flow data for each run,
- fixed gas results from the proposed EPA 18 samples, and
- hydrocarbon results from the Byron, Proposed EPA 18 and EPA 25 methods along with the totals from the off-site hydrocarbon speciation analyses.

A summary of average values under each test condition is given in Table 7-2.

7.1.1 Volatile Organic Carbon (VOC) Measurements

Three independent sampling and five different analytical techniques were used to measure the VOC remaining after incineration. These procedures which have been discussed earlier included:

- EPA Method 25,
- proposed EPA Method 18 including on-site and detailed off-site analyses, and
- Byron Instruments Method which included a direct total hydrocarbon (THC) analysis along with the oxidative/reductive steps to obtain NMHC.

The results of these analyses are shown in Table 7-1 under the heading of Hydrocarbons. All of these results are for the Waste Heat Boiler Outlet (BO) unless otherwise noted under Method 18.

The first, readily apparent, observation is that the proposed Method 18 (on-site and off-site) results and the two types of measurements made by the Byron Method gave similar values. The average and standard deviations overlap in most cases.

TABLE 7-2. INCINERATOR DATA SUMMARY - AVERAGE VALUES FOR EACH SET OF INCINERATOR CONDITIONS

Date	10/22	10/26	10/26*	10/27	10/27	10/27	10/27
Sample Location (1)	RO	RO	RO	RO	WG	RO	WG
Process Data Fuel							
Condition (1)	AW/NG	AW/NG	AW/NG	AW/NG/WG	AW/NG/WG	AW/NG/WG	AW/NG/WG
Incinerator Temp. (°F)	1800	1600	2000	1600	1600	1800	1800
N ₂ Flow (x1000 SCFH)	6.3±0.1	4.8±0.6	5.2	6.25±0.07	6.25±0.07	6.2±0.0	6.2±0.0
Natural Gas Flow (x3500 SCFH)	2.6±0	3.3±0.1	7.5	4.25±0.35	4.25±0.35	5.75±0.07	5.75±0.07
Fixed Gases							
Method 18							
CO ₂ %	5.32±0.14	4.73±0.13	6.75	4.62±0.04	0±0	6.18±0.78	0±0
CO%	0±0	0±0	0	0±0	0±0	0±0	0±0
N ₂ %	81.35±0.30	81.70±0.18	83.0	82.5±0.2	94.83±1.03	82.75±0.57	95.38±0.46
O ₂ %	14.28±0.20	15.03±0.18	12.05	14.98±0.04	1.54±1.21	13.45±0.07	2.08±1.01
Volumetric Flow							
SO Temp. (°F)	126±6	127±0	133	128		132±1.4	
Bar. Pressure ("Hg)	30.4±0.0	30.5±0.0	30.5	30.5		30.5±0.0	
ΔP ("H ₂ O)	0.31±0.00	0.165±0.007	0.15	0.15		0.15±0.00	
Velocity (fps)	33±0	24.5±0.7	23	23		23±0	
ACFM	39200±420	28450±640	27,300	27,200		27,300±0	
SCFM (dry)	30500±710	22050±490	20,400	21,000		20,550±210	
% Moisture	13.5±2.1	14±0	16	14		15.5±0.7	
Hydrocarbons							
Method 18							
RO (ppm - C ₂ -C ₆)	4.98±2.0	<1.0	1.6	<1.0		<1.0	
WG (vol.% - C ₂ -C ₆)					10±6.3		7.57±0.27
NG (vol.% - CH ₄)							
(vol.% - C ₂ -C ₆)							
Byron 401 ppmv-C)							
THC (w/ascarite)	8.5±3.5	2.2±1.1	2.9	1.4±0.1		1.7±0.6	
THC (wo/ascarite)	98		2.1				
NMHC (w/ascarite)	8.5±3.5	2.1±1.2(2)	1.0	1.55±0.07		1.1±0.5	
NMHC (wo/ascarite)	123		2.1(2)				
CO (w/ascarite)	57±3	<0.5	2.0	6±0		2.7±0.8	
CO (wo/ascarite)	315		0.7				
Method 25							
NMHC	1,230±1390	440±390	1806	143±56		93.8±201	
Speciated HIC							
		0.84					

(Continued)

(1) AW - Atactic Waste, NG = Natural Gas, WG = Waste Gas, RO = Waste Heat Boiler Outlet

(2) Difficulties with analysis, value given represents probable concentration.

*Single determination. Therefore, no error limits.

TABLE 7-2. (CONTINUED)

Date	10/28	10/28	10/28	10/28	10/29	10/29	10/26,29
Sample Location (1)	RO	WG	RO	WG	RO	WG	NG
<u>Process Data</u>							
Fuel Condition (1)	AW/NG/WG	AW/NG/WG	NG/WG	NG/WG	NG/WG	NG/WG	AW/NG
Incinerator Temp. (°F)	2000	2000	1800	1800	1600	1600	1800+200
N ₂ Flow (x1000 SCFH)	6.05±0.07	6.1±0.0	6.1±0.0	6.1±0.6	4.0±0.0	4.0±0.0	4.8±0.7
Natural Gas Flow (x3500 SCFH)	7.65±0.07	7.65±0.07	>10	>10	9.3±0.0	9.3±0.0	7.4±1.9
<u>Fixed Gases</u>							
Method 18							
CO ₂ %	6.46±0.09	0±0	4.76±0.00	0±0	4.53±0.61	0±0	1.11±0.54
CO%	0±0	0±0	0±0	0±0	0±0	0±0	0±0
N ₂ %	83.55±0.14	93.8±0.7	83.3±0.1	95.18±0.53	82.8±0.8	95.4±0.1	0±0
O ₂ %	11.78±0.18	2.21±0.01	13.4±0.1	0.90±1.12	14.63±0.18	0.31±0.34	0±0
<u>Volumetric Flow</u>							
SO Temp. (°F)	135.5±0.7		135.5±2.1		133.5±0.7		
Rar. Pressure ("Hg)	30.5±0.0		30.5±0.0		30.5±0.0		
ΔP ("H ₂ O)	0.14±0.00		0.125±0.007		0.125±0.007		
Velocity (fps)	22±0		21.5±0.7		21.5±0.7		
ACFM	26,400±0		24,950±640		24900±710		
SCFM (dry)	19,350±210		18,400±850		18,600±570		
% Moisture	17.5±0.7		17±1.4		16±0		
<u>Hydrocarbons</u>							
Method 18							
RO (ppm - C ₂ -C ₆)	<1.0		<1.0		<1.0		
WG (vol.% - C ₂ -C ₆)		10.82±1.33		9.36±1.90		10.83±3.40	
NG (vol.% - CH ₄)							76.2±0.7
(vol.% - C ₂ -C ₆)							9.46±5.11
<u>Byron 401 (ppmv-C)</u>							
THC (w/ascarite)	2.8±0.7		1.1±0.6		0.9±0.4		
THC (wo/ascarite)							
NMHC (w/ascarite)	1.3±0.8		0.7±0.5		0.49±0.02		
NMHC (wo/ascarite)							
CO (w/ascarite)	1.6±2.2		2.3±2.3		1.25±0.02		
CO (wo/ascarite)							
<u>Method 25</u>							
NMHC	69.6±0.2		129±89		143±18		
<u>Speciated HC</u>							
					0.49±.07		

(1) AW - Attactive Waste, NG = Natural Gas, WG = Waste Gas, RO = Waste Heat Roller Outlet

(2) Difficulties with analysis, value given represents probable concentration.

*Single determination. Therefore, no error limit.

The Method 25 values for VOC from the Boiler Outlet are 100 to 1000 times greater than the other methods. This difference suggests that the Method 25 data do not represent true values and there is an inherent problem with the method when applied to combustion processes. A problem which may be similar occurred with the Byron Instruments method. During the separations, the CO₂ would bleed into the peak areas of the hydrocarbons because of its high value (~5%). Ascarite was used to scrub the samples of CO₂ before they were analyzed by the Byron 401. This problem and solution are discussed in much more detail in Appendix D.

A second observation of the data is also readily seen. During 10/21 and the first test during 10/22, the VOC content of the Boiler Outlet was much higher than during the rest of the project. This resulted from a process control malfunction of the meter which indicated the ratio between combustion air and quench air. There was not enough combustion air and too much quench air. ARCO personnel worked over the weekend of 10/23 and 10/24 to rectify this problem. Many compounds were seen during the on-site hydrocarbon analyses during this upset period. Furthermore, it was observed that the flame color in the incinerator was a dark orange during this period while the flame was a bright yellow during proper operation.

Lastly, during the analyses by the proposed Method 18 and Byron 401, there was no methane observed. This indicates that what little VOC's were measured are potentially reactive organics in ozone formation. Attempted identifications of these low level species are contained in the next section.

7.1.2 Hydrocarbon Speciation Results

Three samples including a duplicate sample for hydrocarbon speciation were obtained from the proposed Method 18 samples. The results of these analyses are listed in Table 7-3.

TABLE 7-3. HYDROCARBON SPECIATION OF BOILER
OUTLET SAMPLES (ppbv-C)

COMPOUND	AW/NG, 1600°F 10/26, 1145 B.O.	NG/WG, 1600°F 10/29, 0858 B.O.	NG/WG, 1600°F 10/29, 0858 B.O.
Ethane	25.3	-	26.5
Propane	42.7	-	-
Propylene	-	20.4	28.4
Propyne	26.6	-	8.0
Unknown #29	54.3	16.0	21.9
Isobutane	26.6	10.5	-
Isobutene	29.8	26.6	10.8
Butane	-	9.2	9.2
1-Pentene	21.6	-	7.9
2-Methyl-1-Butene	18.3	21.7	-
Pentane	15.8	18.9	13.1
2-Methyl-2-Butene	57.2	-	-
cis-2-Pentene	-	33.1	52.4
Neohexane	-	-	28.3
Isobutyraldehyde	-	15.1	-
3-Methylpentane	17.0	-	-
Methylcyclohexane	13.5	-	-
Hexane	-	221.7	-
Benzene	-	19.0	-
Toluene	136.1	45.4	29.0
Octane	25.1	8.2	10.3
Unknown #2	-	6.2	-
Unknown #44	33.4	6.4	12.7
m-Xylene	44.8	15.2	20.6
Unknown #106	-	-	6.3
Styrene	15.1	6.2	7.5
o-Xylene	16.8	-	8.3

TABLE 7-3. (Continued)

	AW/NG, 1600 F 10/26/, 1145 B.O.	NG/WG, 1600 F 10/29, 0858 B.O.	NG/WG, 1600 F 10/29, 0858 B.O.
Nonane	40.9	15.4	18.9
α -Pinene	16.7	6.2	8.2
p-Ethyltoluene	14.1	5.8	6.6
Unknown #19	-	-	10.4
β -Pinene	27.6	6.8	5.5
1,2,4-Trimethylbenzene	18.4	6.7	6.6
1-Decene	45.0	-	-
p-Isopropyltoluene	14.0	-	16.9
Unknown #52	13.0	-	-
Decane	-	21.6	25.8
Undecane	28.8	11.4	11.7
Ethylbenzene	-	-	5.5
TOTAL (TNMHC)	838.5	537.7	437.3
% IDENTIFIED	88.0%	95.0%	88.3%

The total non-methane hydrocarbons are about what was observed during the on-site analyses by the Byron 401 and gas chromatographic method (EPA Method 18). Furthermore, the totals indicate that the higher concentrations of hydrocarbons were found when the atactic waste was being incinerated. Many of the compounds are of questionable identification due to their low levels and blank interferences. However, fourteen of the same compounds occurred in all three samples.

7.1.3 Fixed Gases

Table 7-2 presents average values obtained for fixed gas analysis during the various burn conditions. From these analyses, the percent excess oxygen for each condition was calculated. These results are given in Table 7-4. Example calculations are discussed in Section 7.4.2. The overall average excess O₂ is 172%. As the temperature of the incinerator was increased, the excess oxygen decreased. This occurrence was as expected and demonstrates that with a relatively constant air flow into the incinerator, more oxygen is consumed at higher temperatures (higher fuel rates). The different fuel mixtures generally do not appear to affect the excess oxygen.

Fixed gas analyses of the boiler outlet accounted for approximately 100% of the gases in all tests.

7.1.4 BGI Filters

Table 7-5 presents the results of the organic analysis of three of the BGI particulate filters. This table shows that all of the volatile organics (as TCO) are all less than the blank, and the organics which were measured are considered to be those with a boiling point greater than 300°C (GRAV). Because of the high molecular weight of the compounds found, they have been considered to be non-volatile and hence are not included in any of the calculations for destruction efficiencies.

TABLE 7-4. PERCENT EXCESS OXYGEN FOR EACH
SET OF OPERATING CONDITIONS

Incinerator Conditions	% Excess Oxygen	Average Excess O ₂
AW/NG @ 1600°F	223%	212%
NG/WG @ 1600°F	198%	
AQ/NG/WG @ 1600°F	215%	
AW/NG @ 1800°F	193%	168%
NG/WG @ 1800°F	153%	
AQ/NG/WG @ 1800°F	157%	
AW/NG @ 2000°F	120%	117%
Aw/NG/WG @ 2000°F	113%	
OVERALL AVERAGE		172%

TABLE 7-5. RESULTS OF ORGANIC ANALYSIS OF BGI FILTERS

Conditions	TCO	GRAV	Total Extractable Organics
AW/NG 1800°F	Less than Blank	0	Less than Blank
AW/NG 1600°F	Less than Blank	1800 total µg 44,400 µg/Nm ³	1800 total µg 44,400 µg/Nm ³
AW/NG/WG 2000°F	Less than Blank	600 total µg 24,100 µg/Nm ³	600 total µg 24,100 µg/Nm ³
Blank	66 total µg	400 total µg	

7.2 Total Organic Carbon (TOC) Analyses of Aqueous Condensate

TOC analyses were performed on the aqueous condensate to determine the amount of volatile carbon which was not collected in the bag/drum sampling apparatus. Table 7-6 shows the amount of TOC which was collected for each run. Table 7-7 relates these concentrations to the total volatile carbon determined from bag sampling and impingers. Impinger samples from the boiler outlet generally contained at least 65 percent of the total volatile carbon. The waste gases, however, exhibited a much lower carryover into the impingers. The average concentration of waste gas hydrocarbons in the bag was $\sim 5,400,000 \mu\text{g}/\text{m}^3$ while the impinger TOC content was around $100,000 \mu\text{g}/\text{m}^3$. Because of this large difference, the percent of total carbon due to the impinger catch was very small. Typically, it was less than 2 percent of the total.

7.3 Atactic Waste Analysis

The atactic waste was subjected to ultimate/proximate, heat content and moisture analyses. Table 7-8 presents selected results relative to temperature and fuel conditions. The percentage of carbon in the atactic waste and its heat content (Btu/lb) showed little fluctuation during the testing period. These data show a substantial amount of carbon present in the atactic waste and, consequently, a relatively high heating value associated with it. The low moisture content of the waste also contributes to its high net heat value. Table 7-9 also shows little difference in these parameters for each day of sampling ($\sim 2\%$ for the greatest difference). Complete results of these analyses are contained in Appendix C. A summary of these data is presented in Table 7-10.

7.4 Calculations

7.4.1 Calculation of Destruction Efficiencies

This section explains the parameters required and shows example calculations for the determination of incinerator destruction efficiencies based on four sets of hydrocarbon data. The calculations presented (for

TABLE 7-6. TOC LEVELS IN IMPINGER CATCHES*

SAMPLE #	TOC	VOL (m ³) @ 25°C	µg TOC/m ³	VOL (SCF) @ 60°F	µg TOC/SCF
002	20,800±184	.0428	4.86E5±4.29E3	1.46	1.42E4±1.26E2
015 or 011**	1,925±70.7	.0425	4.53E5±1.66E3	1.45	1.33E3±4.88E1
021	350±70.7	.0431	8.12E3±1.64E3	1.47	2.38E2±4.81E1
024	225±70.7	.0412	5.46E3±1.72E3	1.41	1.60E2±5.01E1
027	<BL	.0385	<BL	1.32	<BL
033	25±70.7	.0405	6.17E2±1.75E3	1.38	1.81E1±5.12E1
038	41,175±70.7	.0437	9.42E5±1.62E3	1.49	2.76E4±4.75E1
044	50±70.7	.0340	1.47E3±2.08E3	1.16	4.31E1±6.10E1
049	75±70.7	.0328	2.29E3±2.16E3	1.12	6.70E1±6.31E1
054	<BL	.0330	<BL	1.13	<BL
057	<BL	.0384	<BL	1.31	<BL
067	25±70.7	.0436	5.73E2±1.62E3	1.49	1.68E1±4.75E1
078	75±70.7	.0407	1.84E3±1.74E3	1.39	5.40E1±5.09E1
084	1,100±86.6	.0249	4.42E4±3.48E3	0.849	1.30E3±1.02E2
090	150±70.7	.0357	4.20E3±1.98E3	1.22	1.23E2±5.80E1
091	35,926±70.7	.0408	8.81E5±1.73E3	1.40	2.57E4±5.05E1
098	41,925±70.7	.0382	1.10E6±1.85E3	1.31	3.20E4±5.40E1
100	50±70.7	.0286	1.75E3±2.47E3	0.979	5.12E1±7.22E1
103	50±70.7	.0254	1.97E3±2.78E3	0.867	5.77E1±8.16E1
108	38,675±70.7	.0394	9.82E5±1.79E3	1.35	2.86E4±5.24E1
112	50±70.7	.0317	1.58E3±2.23E3	1.08	4.63E1±6.55E1
117	50±70.7	.0339	1.47E3±2.09E3	1.16	4.31E1±6.10E1
120	27,675±70.7	.0373	7.42E5±1.90E3	1.28	2.16E4±5.52E1
123	19,300±1592	.0400	4.83E5±3.98E4	1.37	1.41E4±1.16E3

* Error limits based on instrument error. VOL (SCF) = VOL (m³) x 34.1 SCF/m³
aEb = a x 10^b

** Two sample numbers for the same sample.

TABLE 7-7. IMPINGER CATCH TOC VS. TOTAL SAMPLE TOC

Operating Conditions and Sampling Point	Impinger Catch TOC $\mu\text{g}/\text{m}^3$	Total VOC (Impinger and Bag) $\mu\text{g}/\text{m}^3$	Impinger % of Total VOC
AW/NG-BO 1800°F	1.96E4±2.9E3	2.23E4±3.09E3	87.9
AW/NG-BO 1600°F	1.04E3±2.72E3*	<1.57E3±2.72E3	>66.2
AW/NG-BO 2000°F	2.29E3±2.16E3	3.15E3±2.16E3	72.6
AW/NG/WG-BO 1600°F	<Blank	<5.35E2	0
AW/NG/WG-WG 1600°F	9.42E5±1.62E3	5.44E7±3.37E7	1.73
AW/NG/WG-BO 1800°F	1.21E3±2.38E3	<1.75E3±2.38E3	>69.1
AW/NG/WG-BO 2000°F	2.42E4±3.98E3	<2.47E4±3.98E3	>98.0
AW/NG/WG-WG 2000°F	8.81E5±1.73E3	5.88E7±7.12E6	1.50
NG/WG-BO 1800°F	1.86E3±3.72E3	<2.4E3±3.72E3	>77.5
NG/WG-WG 1800°F	1.04E6±2.57E3	5.11E7±1.02E7	2.04
NG/WG-BO 1600°F	1.53E3±3.05E3	<2.07E3±3.05E3	>73.9
NG/WG-WG 1600°F	6.13E5±3.98E4	5.85E7±1.82E7	1.05

*Average of two determinations, one determination was <Blank.
 $a_{eb} = a \times 10^b$

TABLE 7-8. PERCENT CARBON, BTU/LB AND PERCENT MOISTURE IN ATACTIC WASTE FOR EACH SET OF OPERATING CONDITIONS

Fuel Conditions			Temperature	Percent Carbon	Btu/lb (Gross)	Percent Moisture
AW	NG	WG				
X	X		1800	76.67 ± 0.79	18848 ± 043	---
X	X		1600	75.81 ± 0.35	18437 ± 057	0.05 ± 0
X	X		2000	$75.84 \pm 0.19^*$	$18503 \pm 003.5^*$	$0.095 \pm 0.007^*$
X	X	X	1600	75.56 ± 0.09	18338 ± 086	0.12^{**}
X	X	X	1800	75.63 ± 0.19	18570 ± 042	$0.19 \pm 0.028^*$
X	X	X	2000	75.95 ± 0.35	18656 ± 036	0.30^{**}
OVERALL AVERAGE				75.96 ± 0.56	18576 ± 190	0.13 ± 0.096

*One sample, Two determinations

**One determination

TABLE 7-9. AVERAGE BTU/LB, PERCENT CARBON AND PERCENT MOISTURE
IN ATACTIC WASTE FOR EACH DAY OF SAMPLING

Dates	10/22/81	10/26/81	10/27/81	10/28/81
Average Btu/lb. (Gross)	18848±043	18454±057	18453±145	18656±036
Average % Carbon	76.67±0.79	75.82±0.29	75.59±0.13	75.95±0.30
Average % Moisture (Karl Fisher Method)		0.065±0.03	0.155±0.05	0.30**

**One determination.

TABLE 7-10. RESULTS OF PROXIMATE, ULTIMATE, Btu CONTENT
AND MOISTURE ANALYSES FOR ATACTIC WASTE

	Sample Description						
	AW/NG 1600°F			AW/NG 1800°F			AW/NG 2000°F
	020* (10/26;0926)	032 (10/26;0914)	055* (10/26;1645)	013 (10/22;0916)	014 (10/22;1310)	031 (10/22;1616)	048 (10/26;1645)
<u>Proximate Analysis</u> [†]							
% Moisture	X	0.05	0.10 ± 0.007	X	X	0.05	X
% Ash	0.59	0.77	0.73 ± 0.007	0.56	0.53	0.62	0.49
% Volatile	99.41	99.18	99.18 ± 0.0	99.44	99.47	99.33	99.51
% Fixed Carbon	0.00	0.00	0.0	0.00	0.00	0.00	0.00
<u>Ultimate Analysis</u> [†]							
% Moisture	X	0.05	0.10 ± 0.007	X	X	0.05	X
% Carbon	75.89	75.40	75.84 ± 0.19	77.58	76.81	76.25	76.11
% Hydrogen	13.01	12.89	12.91 ± 0.02	12.86	12.95	12.80	12.69
% Nitrogen	0.28	0.09	0.14 ± 0.01	0.20	0.17	0.13	0.19
% Chlorine	0.34	0.58	0.57 ± 0.02	0.31	0.56	0.26	0.17
% Sulfur	0.59	0.14	0.23 ± 0.11	0.15	0.53	0.36	0.49
% Ash	0.35	0.61	0.73 ± 0.007	0.56	0.34	0.62	0.22
% Oxygen (by difference)	9.54	10.24	9.52 ± 0.06	8.34	9.27	9.53	10.13
Btu/lb (Gross)	18391	18419	18503 ± 3.5	18824	18898	18822 0.05	18501
% Moisture (Wt. %)		0.05	0.10 ± 0.007				

* Samples recorded in log improperly

† All results on "as received" basis.

TABLE 7-10. (CONTINUED)

	Sample Description					
	AW/NG/WG 1600°F		AW/NG/WG 1800°F		AW/NG/WG 2000°F	
	039 (10/27;1027)	070 (10/27;1330)	077 (10/27;1540)	079 (10/27;1735)	043 (10/28;1004)	092 (10/28;1158)
<u>Proximate Analysis</u> [†]						
% Moisture	0.12	X	0.19 ± 0.03	X	X	0.30
% Ash	0.68	0.81	0.73 ± 0.02	0.55 ± 0.18	0.72	0.83
% Volatile	99.20	99.19	99.09 ± 0.007	99.45 ± 0.18	99.28	98.87
% Fixed Carbon	0.00	0.0	0.0	0.0	0.00	0.00
<u>Ultimate Analysis</u> [†]						
% Moisture	0.12	X	0.19 ± 0.03	X	X	0.30
% Carbon	75.49	75.62	75.76 ± 0.13	75.49 ± 0.04	75.70	76.19
% Hydrogen	12.98	12.71	12.90 ± 0.08	13.01 ± 0.11	12.98	13.18
% Nitrogen	0.41	0.21	0.15 ± 0.0	0.19 ± 0.03	0.20	0.24
% Chlorine	0.60	0.35	0.55 ± 0.09	0.56 ± 0.04	0.54	0.61
% Sulfur	0.24	0.81	0.24 ± 0.12	0.28 ± 0.02	0.27	0.32
% Ash	0.68	0.28	0.73 ± 0.02	0.55 ± 0.18	0.75	0.83
% Oxygen (by difference)	9.48	10.02	9.50 ± 0.01	9.94 ± 0.04	9.56	8.33
Btu/lb	18399	18277	18600 ± 17	18540 ± 62	18630	18681
% Moisture (Wt. %)	0.12		0.19 ± 0.028			0.30
NO _x						

* Samples recorded in log improperly.

† All results on "as received" basis.

AW/NG/WG at 2000°F) are representative of the calculations used to generate Table 2-1 in Section 2.1. All data used in these calculations are taken from Tables 7-2 and 7-6.

First the carbon mass flow rates for inlet and outlet streams must be determined. The flow rates for waste gas and natural gas inlet streams and the stack gas outlet stream were calculated directly. The carbon flow into the incinerator was calculated for waste gas and natural gas. The carbon mass flow rate in the waste gas, the waste gas flow rate and the pounds of carbon per standard cubic foot in the waste gas were calculated as shown in Equations A and B. Then the pounds of carbon per hour attributable to the waste gas was calculated (Equation C). Although the total organic carbon (TOC) determined in the aqueous condensate impinger catches generally contributed a negligible amount to the total carbon, it was included for completeness. These calculations are shown in Equations D and E. The impinger contribution was then added to the amount of carbon determined in C to give the total carbon flow rate of the waste gas (Equation F). These same calculations were applied to the natural gas, except there was no impinger contribution and the flow rate was taken from process data (Equations G, H and I).

The carbon flow rate out of the incinerator was calculated from the stack gas emissions. This was determined again following the procedures as for waste gas with the impinger contribution (Equations J, K and L) using CO₂ as the major carbon-containing species. The stack gas flow rate was measured on-site.

Since the flow rate of the atactic waste could not be measured directly, the carbon flow rate was estimated from the carbon flow rates of the waste gas, natural gas and stack gas (Equation M). Using the results of the ultimate analysis of the atactic waste, the flow rate of the atactic waste itself was also estimated (Equation N).

With this information, destruction efficiencies were then calculated. Paragraph O shows the hydrocarbon determinations taken from Table 7-2 for each method, represented as percent carbon. Equations P and Q show the equations for calculation of destruction efficiencies and Sections 1 through 4 carry these calculations through for each method of hydrocarbon determination.

For operating conditions where the atactic waste was not used to fuel the incinerator, a carbon balance around the incinerator was attempted. These data are shown in Table 7-11.

7.4.2 Calculation of Excess Oxygen

The percent excess oxygen was calculated in order to determine the amount of oxygen remaining after stoichiometric combustion of the waste products. This section discussed the calculations required to determine excess oxygen. All data used in the calculations were taken from Table 7-2.

To calculate the excess oxygen, the O_2 flow into the incinerator must first be determined. This was done indirectly since no empirical measurements were available. The N_2 flow due to combustion air first calculated from the total stack flow and the N_2 flow from the waste gas (R). This value was used to then obtain total air flow in (S) and from that O_2 flow into the incinerator (T). Oxygen flow out of the incinerator must then be calculated. This was easily accomplished as shown in U. From these parameters, the oxygen consumed in combustion (V) and the percent of excess oxygen (W) were calculated.

7.5 Miscellaneous Analyses

Other analyses which were done were not required for the determination of destruction efficiencies. These analyses discussed below, were accomplished to gain better insight into the composition of the stack gas.

7.5.1 Inorganic Species

Table 7-12 presents results from the analyses of the aqueous condensate in the impinger catches from a boiler outlet sample. These data characterize this condensate as relatively acidic, and give an indication of what acid gases (pH=3.1) may be present in the gas stream. The NaOH impinger contains primarily dissolved CO₂. If this represents about 4.5% CO₂ as determined from fixed gas analysis, all other species determined are <0.05% by volume.

7.5.2 NO_x

Table 7-13 summarizes the results of the NO_x data obtained for each set of incineration conditions. The highest value of NO_x occurred for the fuel mixture of waste gas, natural gas and atactic waste at 2000°F. Within two standard deviations (95% confidence interval) all other conditions have the same NO_x levels.

EXAMPLE CALCULATIONS

AW/NG/WG @ 2000°F

INLET STREAMS

$$A. \text{ Waste Gas flow rate (WGFR)} = \frac{\text{Nitrogen Flow Rate in (NFRI)}}{\text{Waste Gas \% N (WGN)}} \times 100$$

$$= \frac{6100 \pm 0}{93.8 \pm 0.7} \times 100 = 6503 \pm 48 \text{ SCFH}$$

$$\text{WGN} = 93.8\% \pm 0.7\%$$

$$\text{NFRI} = 6100 \pm 0 \text{ SCFH}$$

$$B. \text{ LBS C/SCF in WG} = \frac{\text{Waste Gas \% C (WGC)/100}}{0.8493 \text{ ft}^3/\text{mole}} \times \frac{12 \text{ g/mole}}{454 \text{ g/lb}}$$

$$= \frac{10.82 \pm 1.33/100}{0.8493} \times \frac{12}{454} = 3.37\text{E-}3 \pm 4.\text{E-}4 \text{ LBS C/SCF}$$

$$\text{WGN} = 10.82\% \pm 1.33\%$$

$$C. \text{ LBS C in WG/HR} = \text{WGFR} \times \text{LBS C/SCF in WG}$$

$$= (6503 \pm 48) (0.00337 \pm 4\text{E-}4) = 21.9 \pm 2.6$$

$$D. \text{ LBS C/SCF in Impinger} = \text{TOC} \left(\frac{\mu\text{g}}{\text{m}^3} \right) \times \frac{\text{m}^3}{34.1 \text{ SCF}} \times \frac{\text{g}}{10^6 \mu\text{g}} \times \frac{\text{LB}}{454 \text{ g}}$$

$$= 8.81\text{E}5 \pm 1.73\text{E}3 \mu\text{g/m}^3 \times \frac{\text{m}^3}{34.1 \text{ SCF}} \times \frac{\text{g}}{10^6 \mu\text{g}} \times \frac{\text{LB}}{454 \text{ g}}$$

$$= 5.69\text{E-}5 \pm 1.12\text{E-}7 \text{ LBS C/SCF}$$

$$E. \text{ Impinger Contribution} = (\text{LBS C/SCF}) (6503 \pm 48 \text{ SCFH})$$

$$(5.69\text{E-}5 \pm 1.12\text{E-}7 \text{ LBS C/SCF}) (6503 \pm 48 \text{ SCFH}) = 0.37 \pm 0.0028$$

$$F. \text{ Total LBS C/HR} = \text{LBS C/HR in WG} + \text{Impinger Contribution (LBS C/HR)}$$

$$= (21.9 \pm 2.6) + (0.37 \pm 0.0028) = 22.3 \pm 2.6$$

$$G. \text{ LBS C/SCF in Natural Gas (NG)} = \frac{\text{Natural Gas \% C (NGC)}/100}{.8493 \text{ ft}^3/\text{mole}} \times \frac{12 \text{ g/mole}}{454 \text{ g/lb}}$$

$$\begin{aligned} \text{NGC} &= 76.2 \pm .7 \% \text{ C from CH}_4 \\ &+ 9.46 \pm 5.11 \% \text{ C from C}_2 - \text{C}_6 \\ &\underline{85.66 \pm 5.16 \% \text{ C Total}} \end{aligned}$$

$$H. \text{ LBS C/SCF NG} = \frac{85.66 \pm 5.16 /100}{.8493} \times \frac{12}{454} = .0267 \pm .0016$$

$$I. \text{ LBS C NG/HR} = \text{Natural Gas Flow Rate (NGFR)} \times \text{LBS C/SCF NG}$$

$$= (26,800 \pm 245. \text{ SCFH})(.0267 \pm .0016 \text{ LBS C/SCF}) = 716 \pm 43$$

OUTLET STREAM

$$J. \text{ LBS C Stack Gas (SG)} = \frac{\text{Stack Gas Total Carbon (SGTC)}/100}{.8493 \text{ ft}^3/\text{mole}} \times \frac{12 \text{ g/mole}}{454 \text{ g/lb}}$$

$$= \frac{6.46 \pm .09/100}{.8493} \times \frac{12}{454} = 2.01 \text{ E-3} \pm 2.8 \text{ E-5 LBS C/SCF}$$

$$\text{SGTC} = 6.46\% \pm .09\%$$

$$\text{LBS C/SCF Impinger} = 1.56\text{E-6} \pm 2.57\text{E-7} \text{ (calculated same way as for WG)}$$

$$K. \text{ TOTAL LBS C} = \text{LBS C in SG} + \text{LBS C in Impinger}$$

$$= (2.01\text{E-3} \pm 2.8\text{E-5}) + (1.56\text{E-6} \pm 2.57\text{E-7})$$

$$= 2.011\text{E-3} \pm 2.8\text{E-5}$$

$$\begin{aligned}
 \text{L. } \frac{\text{LBS } C_{\text{SG}}}{\text{HR}} &= \text{Stack Gas Flow Rate (SGFR)} \times \text{Total LBS C/SCF SG} \\
 &= (116100 \pm 12600 \text{ SCFH}) (2.01\text{E-}3 \pm 2.8\text{E-}5) = 2334 \pm 41 \text{ LBS C/HR} \\
 &\quad \text{SGFR} = 19,350 \text{ SCFM} \times 60 \frac{\text{MIN}}{\text{HR}} \\
 &= 1161000 \text{ SCFH}
 \end{aligned}$$

M. LBS C ATACTIC WASTE

$$\begin{aligned}
 \frac{\text{LBS } C \text{ ATACTIC WASTE}}{\text{HR}} &= \text{LBS } C_{\text{SG}} - \left[\frac{\text{LBS } C_{\text{NG}}}{\text{HR}} + \frac{\text{LBS } C_{\text{WG}}}{\text{HR}} \right] \\
 &= (2334 \pm 41) - [(716 \pm 43) + (22.3 \pm 2.6)] \\
 &= 2334 \pm 41 - (738 \pm 43) = 1596 \pm 59 \text{ LBS C/HR}
 \end{aligned}$$

N. LBS ATACTIC WASTE

$$\begin{aligned}
 &= \frac{1596 \pm 59 \text{ LBS C in Atactic Waste}}{.7596 \pm .0056 \% \text{ C in Atactic Waste (from ultimate analyses)}} \\
 &= 2101 \pm 79 \text{ LBS Atactic Waste/HR}
 \end{aligned}$$

DESTRUCTION EFFICIENCIES

$$\begin{aligned}
 \text{O. GCHC} &< 1.0 \text{ ppm-C} &= < 1.0\text{E-}4 \% \\
 \text{Byron-THC} &2.8 \pm 0.7 \text{ ppm-C} &= 2.8\text{E-}4 \pm 0.7\text{E-}4\% \\
 \text{Byron-NMHC} &1.3 \pm 0.8 \text{ ppm-C} &= 1.3\text{E-}4 \pm 0.8\text{E-}4\% \\
 \text{Method 25} &= 69.6 \pm 0.2 \text{ ppm-C} &= 6.96\text{E-}3 \pm 0.2\text{E-}4\%
 \end{aligned}$$

$$\text{P. } \% \text{ Destruction Eff} = 100 - \left[\frac{1\text{bs SGVOC/HR}}{1\text{bs } C_{\text{AW}}/\text{HR} + 1\text{bs } C_{\text{WG}}/\text{HR}} \times 100 \right]$$

Q. LBS Stack Gas Volatile Organic Carbon (SGVOC)/HR =

$$\begin{aligned}
 &\text{SGFR} \times \frac{\text{SGVOC}}{100} \times \frac{12 \text{ g/mole}}{454 \text{ g/lb}} \\
 &\quad .8493 \text{ ft}^3/\text{mole}
 \end{aligned}$$

$$1.) \quad \text{by GCHC} \quad \text{LBS SGVOC} = (116100 \pm 12600 \text{ SCFH}) \times \frac{<1.0\text{E-4}}{.8493} / 100 \times \frac{12}{454}$$

$$= < .0361$$

$$\% \text{ Destruction Eff} = 100 - \left[\frac{< .0361}{(1596 \pm 59) + (22.3 \pm 2.6)} \times 100 \right]$$

$$= 100 - \left[\frac{< .0361}{1618 \pm 59} \times 100 \right] = 100 - (2.23\text{E-3} \pm 8.13\text{E-5})$$

$$= > 99.99777 \pm .00008$$

2.) by BYRON-THC

$$\text{LBS SG}_{\text{VOC}} = (1161000 \pm 12600 \text{ SCFH}) \frac{(2.8\text{E-4} \pm .7\text{E-4})}{\frac{100}{.8493}} \times \frac{12}{454} = .1012 \pm .0253$$

$$\% \text{ Destruction Eff} = 100 - \left[\frac{.1012 \pm .0253}{1618 \pm 59} \times 100 \right]$$

$$= 100 - (6.25\text{E-3} \pm 1.58\text{E-3}) = 99.994\% \pm .002\%$$

3.) by BYRON-NMHC

$$\text{LBS SG}_{\text{VOC}} = (1161000 \pm 12600 \text{ SCFH}) \frac{(1.3\text{E-4} \pm 0.8\text{E-4})}{.8493} / 100 \times \frac{12}{454} =$$

$$.0470 \pm .0290$$

$$\% \text{ Destruction Eff} = 100 - \left[\frac{.0470 \pm .0290}{1618 \pm 59} \times 100 \right]$$

$$= 100 - (2.91\text{E-3} \pm 1.80\text{E-3}) = 99.997\% \pm .002\%$$

4.) by METHOD 25

$$\text{LBS SG}_{\text{VOC}} = (1161000 \pm 12600 \text{ SCFH}) \frac{(6.96\text{E-}3 \pm 0.2\text{E-}4)/100}{.8493} \times \frac{12}{454} = 2.52 \pm .028$$

$$\begin{aligned} \% \text{ Destruction Eff} &= 100 - \left[\frac{2.52 \pm .028}{1618 \pm 59} \times 100 \right] = 100 - (1.56\text{E-}3 \pm 9.6\text{E-}5 \times 100) \\ &= 100 - (.156 \pm .0059) = 99.84\% \pm .01\% \end{aligned}$$

CALCULATION OF EXCESS OXYGEN

$$\begin{aligned} \text{R. } \text{N}_2 \text{ Flow in Stack Gas} &= (\text{volumetric flow (SCFM)} \times \frac{\% \text{ N}_2 \text{ in S.G.}}{100}) - (\text{N}_2 \text{ Flow (SCFH)} / 60 \text{ min/hr}) \\ &= (19350 \text{ SCFM} \times .8355) - (6050 \text{ SCFH} / 60 \text{ min/hr}) = 16070 \text{ SCFM} \end{aligned}$$

$$\text{S. } \text{Air Flow in Stack} = \frac{16070 \text{ SCFM N}_2}{.7808 \text{ (Fraction of N}_2 \text{ in Air)}} = 20580 \text{ SCFM}$$

$$\text{T. } \text{O}_2 \text{ Flow into Stack} = 20580 \text{ SCFM Air} \times .209 \text{ (Fraction of O}_2 \text{ in Air)} = 4300 \text{ SCFM}$$

$$\begin{aligned} \text{U. } \text{O}_2 \text{ Out of Stack} &= \text{Volumetric Flow (SCFM)} \times \frac{\% \text{ O}_2 \text{ in S.G.}}{100} \\ &= (19350 \text{ SCFM} \times .1178) = 2280 \text{ SCFM} \end{aligned}$$

$$\text{V. } \text{O}_2 \text{ Use} = \text{O}_2 \text{ in} - \text{O}_2 \text{ out} = 4300 \text{ SCFM} - 2280 \text{ SCFM} = 202 \text{ SCFM}$$

$$\text{W. } \text{Excess O}_2 = \frac{\text{O}_2 \text{ out}}{\text{O}_2 \text{ use}} \times 100 = \frac{2280 \text{ SCFM}}{2020 \text{ SCFM}} \times 100 = 113\%$$

TABLE 7-11. PROCESS FLOW RATES DURING EACH SET
OF OPERATING CONDITIONS

Conditions	g C Natural Gas/sec (lbs/hr)	g C Waste Gas/sec (lbs/hr)	g C Atactic Waste/sec (lbs/hr)	g Atactic Waste/sec (lbs/hr)	Percent Closure †	g C Stack Gas/sec (lbs/hr)	Production Rate of Steam (x1000 lbs/hr)
AW/NG/WG @ 2,000°F	90.3±5.4 (716±43)	2.77±.33 (22±2.6)	201±7.4 (1596±59)	265±10.0 (2101±79)	- -	294±5.2 (2334±41)	31
AW/NG/WG @ 1,800°F	67.7±4.2 (537±33)	1.93±.069 (15.3±.55)	229±38.1 (1815±302)	301±50.2 (2389±398)	- -	299±37.8 (2367±300)	27.5
AW/NG/WG @ 1,600°F	50±5.1 (397±40.4)	2.6±1.6 (20.8±12.9)	175±5.7 (1384±45.2)	230±7.7 (1822±61)	- -	227±2.0 (1802±15.6)	21.5
NG/WG @ 1,800°F	>118 (>935)	2.3±.54 (18.7±4.3)	- -	- -	- 58%	206±9.5 (1634±75)	25
NG/WG @ 1,600°F	110±6.6 (869±52.1)	1.8±.55 (14.5±4.4)	- -	- -	56.2±8.4	198±27 (1573±217)	20.5
AW/NG @ 2,000°F	88±5.3 (701±42)	- -	236±5.3 (1869±42)	310±7.3 (2460±58)	- -	324 (2570)	33
AW/NG @ 1,800°F	30.6±1.8 (243±14.6)	- -	352±13.6 (2795±108)	464±18.3 (3680±145)	- -	383±13.6 (3038±107)	<35*
AW/NG @ 1,600°F	39±2.6 (308±20.7)	- -	206±9.1 (1637±72)	272±12 (2155±96)	- -	245±8.7 (1945±69)	23.5

*Difficulties with analysis - Based on most probable value

$$\text{lbs/hr} \times \frac{1 \text{ hr}}{60 \text{ min}} \times \frac{1 \text{ min}}{60 \text{ sec}} \times \frac{454 \text{ g}}{1 \text{ lb}} = \frac{\text{g}}{\text{Sec}}$$

$$\dagger \text{Percent Closure} = \frac{\text{gC in waste gas} + \text{gC in Natural gas}}{\text{gC in stack gas}} \times 100$$

TABLE 7-12. ARCO INCINERATOR IMPINGER CATCHES - INORGANIC ANALYSIS
OF BOILER OUTLET SAMPLE*

Parameter	Impinger #1 (Dry)	Impinger #2 (100 mL 1N NaOH)	Blank (1N NaOH)
pH	3.1	9.1	12.6
Acidity (as CaCO_3) mg/L	12800	-	-
Alkalinity (as CaCO_3) mg/L	-	49490	56110
HCO_3^- mg/L	-	33950	< 1
CO_3^{2-} mg/L	< 1	15540	1150
Cl^- mg/L	490	100	157
F^- mg/L	0.12	0.12	0.05
NO_3^- (as N) mg/L	12.2	8.4	< 0.1
Total PO_4 (as P) mg/L	0.75	0.52	0.03
SO_4^{2-} mg/L	340	66	4

*Sampling Period: 10/28, 1800 hrs. to 10/29, 0800 hrs.

Fuel: Natural Gas and Waste Gas

Incinerator Temperature: ~ 1700°F

N_2 Flow: ~ 5000 scfh

Natural Gas Flow: ~ 34000 scfh/Comb. Air P: ~ 3.2" H_2O

TABLE 7-13. NO_x RESULTS FOR SELECTED INCINERATOR CONDITIONS

INCINERATOR CONDITIONS	NO _x * μg/Nm ³ (ppm)
AW/NG @ 1800°F	6.08E4±4.17E3 (22.33±1.53)
AW/NG @ 1600°F	6.92E4±1.13E4 (25.40±4.16)
AW/NG/WG @ 1600°F	6.60E4±6.05E3 (24.25±2.22)
AW/NG/WG @ 2000°F	1.05E5±8.31E3 (38.6±3.05)
NG/WG @ 1600°F	5.50E4±4.03E3 (20.20±1.48)

*Average includes results from duplicate analyses of identical samples on the same day and repeated analysis of samples on different days.

REFERENCES

1. Reference Methods. Appendix A to 40 CFR 60. Environmental Reporter. Bureau of National Affairs, Washington, D.D., December 5, 1980.
2. EPA Proposed Method 18, Draft. Personal communication with William Grimley, U.S. EPA, September 9, 1981.
3. Test Methods. Appendix B to 40 CFR 61. Federal Register Vol. 45, No. 77, Friday, April 18, 1980.
4. D.E. Lentzen, D.E. Waggoner, E.D. Estes, and W.F. Gutknecht, IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition), NTIS No. Pb-293-795 Research Triangle Institute, Research Triangle Park, NC, October 1978.