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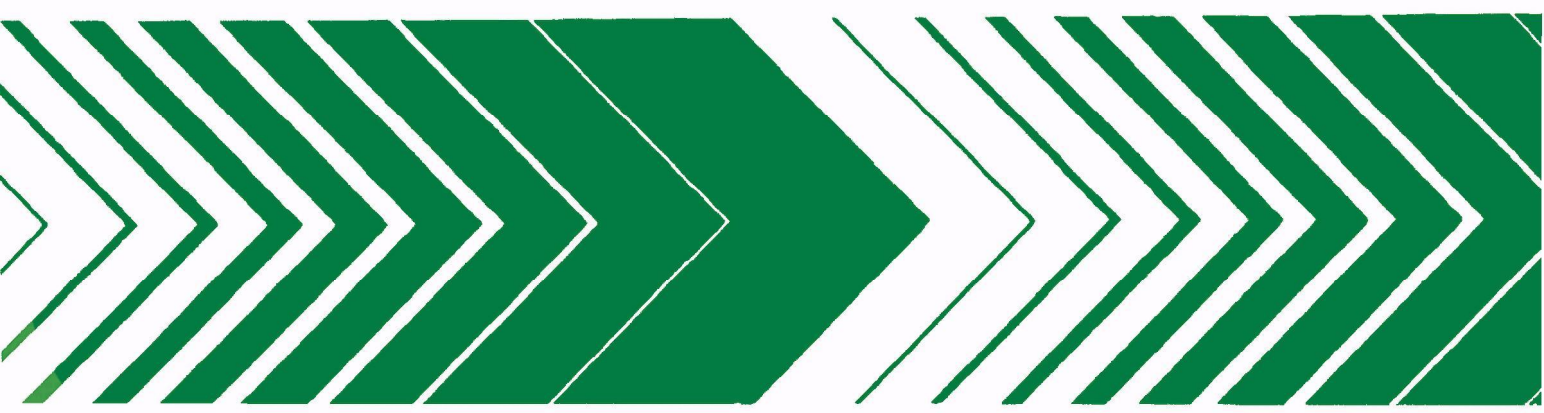
EPA/IERL-RTP Procedures Manual: Level 2 Sampling and Analysis of Selected Reduced Inorganic Compounds



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EPA/IERL-RTP Procedures Manual: Level 2 Sampling and Analysis of Selected Reduced Inorganic Compounds

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Office of Research and Development
Washington, DC 20460

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SECTION 1.0

INTRODUCTION

In the past few years intrest has grown in the determination of specific inorganic compounds being emitted from industrial sources rather than the general determination of total metal emissions. The identification of specific compounds is necessary to throughly assess the environmental impact of a given source. Health effects are generally based on specific compounds not on compound classes which are determined in industrial effluents routinely. The purpose of this study was to develop sampling and analysis techniques for the determination of emission rates of specific reduced inorganic compounds from stationary sources. The report includes a review, of the current literature on sampling and analysis together with methods evaluation in laboratory and field for the sampling and analysis techniques proposed.

For the purpose of this study reduced inorganic compounds are defined as any metal or non-metal which is bound to hydrogen, in its zero oxidation state, or is bound to carbon. A group of industrial categories has been reviewed as to possible emissions of reduced inorganic compounds. Several of the typical effluent streams from these various industrial categories have been identified as candidate sources of reduced inorganic compound emissions based on the chemistry and literature information on the processes. Generalized sampling points have been identified for typical plant operations.

The overall goal of this task was to establish sampling and analysis techniques which can provide for an accuracy of $\pm$25% in the determination of specific reduced inorganic compounds from various industrial sources. A detailed evaluation of the Source Assessment Sampling System (SASS) as a sampling device for reduced inorganic compounds at the trace level was

made and is reported in detail. The results of this evaluation, show the SASS train to be inadequate for sampling and subsequent compound identification of the more reactive reduced inorganic compounds. Many of the species of interest are lost in various parts of the sampling train, or their structure modified in such a way that direct determination of the original emission form cannot be made.

In field sampling applications, analysis of the samples must be conducted remote from the sampling site. Analytical instrumentation which can provide compound identification, especially on highly reactive species, is generally not available at remote locations. Therefore, stability, storage and transport are serious considerations in proposing a sampling and analysis technique. Certain assumptions must be made about many of the streams to be sampled, and the evaluation of potential interferences from a wide variety of sources has not been exhaustively examined. A significantly larger data base is required before the methods proposed in this report can be routinely applied to a wide variety of sources. A thorough examination of possible interferences is also required especially in those instances where mixed reduced and oxidizing streams are encountered.

SECTION 2.0

STREAM PARAMETERS FOR PROCESSES WITH REDUCING STREAMS

The specification of appropriate sampling procedures for any specific chemical requires an understanding of its physical and chemical properties as well as the physical and chemical parameters of the stream in which it may be found. This section provides the required information about process and effluent streams which may contain reduced inorganic compounds by identifying:

1) those industries which may be sources of reduced inorganic species;
2) the specific effluent streams which may contain the species in question and
3) methods which can be used to sample the identified streams.

The data concerning industrial sources of reduced inorganic compounds were gathered from the literature whenever possible. The published information was supplemented by analysis of the chemistry and operating parameters of the individual processes and personal contact with knowledgable individuals.

The results of the effort to identify the pertinent industries and effluent streams are described in this section and information concerning sampling methods may be found in Section 3.0.

2.1 SAMPLING STREAM PARAMETERS

For the purpose of this investigation, a reduced inorganic compound has been defined as any metal or non-metal which is bound to hydrogen, is in the zero oxidation state, or is bound to carbon. Unfortunately, the literature contains very few references which identify specific reduced compounds in effluents from industrial processes. Generally, the species cited are relatively common well known compounds such as H_2S, COS,

NH_3 and simple cyanides. Therefore, the literature search was supplemented by an examination of the chemistry and operating conditions of a number of processes which may have the potential to form reduced compounds not commonly considered in source assessment efforts. The following process parameters were selected as likely to be condusive to the formation of reduced species:

- Operations in which hydrogen is present in significant quantity.
- Operations which are oxygen deficient.
- Processes which contain metal oxides in a partially reduced state. Such oxides may interact with various agents to form reduced species. For example, the thermodynamically stable oxidation states of MnO, ZnO, CaO, and V_2O_3 can react with H_2S, within the temperature range of 300°C to 800°C, to form their respective reduced metal sulfides as follows:

$$MnO + H_2S \rightarrow MnS + H_2O$$

$$ZnO + H_2S \rightarrow ZnS + H_2O$$

$$CaO + H_2S \rightarrow CaS + H_2O$$

$$V_2O_3 + 3H_2S \rightarrow V_2S_3 + 3H_2O$$

- Processes which generate substantial quantities of carbon monoxide or nitrogen oxide in the presence of those elements capable of forming carbonyls or nitrosyls.

As a result of the application of these criteria and the literature survey, sixteen processes employed in at least seven industries were identified as potential sources of effluents containing reduced inorganic species. The identified industries are discussed in the following sections and summarized in Table 2-1. The table highlights characteristics of the effluents from the process operations of interest. Following Table 2-1, flow diagrams are presented for eleven of the most important process types along with potential sampling points.

2.2.1 Steel Plants

Hydrogen and hydrogen sulfide have been cited in the literature as

Table 2-1

Industries and Processes Producing Reduced Inorganic Species

Process Idenfication	Effluent Characteristics from Predominant Process Operations					Reduced Species Present in Primary Effluents	
	Particulate Data						
	Size Distribution	gr/SCF	Flow Rate ①	Temperature °F	Moisture: Vol %	Cited From Literature	Probable Stream Based on Chemistry
1) Steel Plant						Ⓖ	Ⓖ
ⓐ Blast Furnace	15-90% < 74μ	4-30, 7-10 avg.	ⓐ 40-140 ⓑ 60-138	390 at throat 3000 at Furnace	9.6	H_2 H_2S	FeS, MgS, MnS COS, CaS, $Fe(CO)_5$, $Mn(CO)_{10}$
ⓑ Sinter Plant	15-45% < 40μ 9-30% < 20μ 4-19% < 10μ 1-10% < 5μ	0.2-3.2	ⓐ 30-460 ⓑ 148-230	100-400	2-10		Ⓖ COS, $Fe(CO)_5$
① Windbox:							Ⓖ
② Discharge end:	80% < 100 10% < 10	1-5	ⓐ 0.03-0.2	100-300			COS, $Fe(CO)_5$
ⓑ Coke Ovens						Ⓖ	Ⓖ
① Oven off gas	Highly Variable	1-15	2.1 M ft^3 per charge	≤1832	Variable depending on point in coking cycle	$Ni(CO)_4$, HCN, NH_3 H_2S, H_2, COS, CS_2, NH_4CN	AsH_3, SbH_3 The formation of a variety of hydrides, carbonyl, and metal sulfides is possible.
						Ⓖ Ⓛ	Ⓖ Ⓛ
② Quench Tower	95-97% > 47μ	0.05-0.1	900 M ft^3 per quench	140-150	Effluent consists primarily of steam	$Ni(CO)_4$, HCN, H_2, NH_3, NH_4CN, COS, CS_2	The formation of a variety of hydrides, carbonyls, and metal sulfides is possible.
						Ⓛ	Ⓛ
③ Sour Quench Water	Not Applicable		Water usually sluiced; flow variable and cyclic			Cyanide and ammonia species are cited in the literature. Distinct compounds are not identified.	Metal sulfides, cyanides, sulfur cyanides, and reduced ammonia species.
2) Coal Fired Boilers	25% < 10 49% < 20 79% < 44	2.9 to 3.7 avg.	ⓐ 297-397 ⓑ 362-434	245-258	6.4	Ⓖ $Cr(CO)_6$ has been cited in the literature, although this is not a reducing atmosphere.	Ⓖ If, however, the formation of $Cr(CO)_6$ is possible, the existence of other carbonyls is also possible. CO concentrations may be as high as 70 ppm.

① Flow rate is expressed in: ⓐ M SCFM or ⓑ M SCF/ton of product processed.

Ⓖ = gaseous phase; Ⓛ = liquid phase; Ⓢ = solid phase

Process Identification	Effluent Characteristics From Predominant Process Operations					Reduced Species Present in Primary Effluents	
	Particulate Data						
	Size Distribution	gr/SCF	Flow Rate	Temperature ^{o}F	Moisture: Vol %	Cited from Literature	Probable Stream Based on Chemistry
Refinery Operations						Ⓖ	Ⓖ Ⓛ
ⓐ Claus Plant Tail Gas						H_2S, COS, CS_2, NH_3, HCN	Spent chemicals from acid gas amine solution regeneration = carbonyls, cyanides, sulfides.
ⓑ Fixed Bed Catalyst Regeneration				Fixed and moving bed regenerable catalysts function at about 850 to 1000°F at 300 to 700 psig		H_2S, COS, CS_2, $Ni(CO)_4$ $[Co(CO)_4]_2$	$Mo(CO)_6$; the formation of various metal sulfides, hydrides and carbonyls probable.
ⓒ Moving Bed Catalyst Regeneration						H_2S, COS, CS_2, NH_3, $Ni(CO)_4$, HCN	
ⓓ Fluid Coker off-gas						H_2S, COS, CS_2, NH_3, RCN, $Ni(CO)_4$	Metal sulfides and carbonyls probable.
Coal Conversion ①							
ⓐ Gasification and Liquefaction Operations						Sulfides in rinse solution and particulate. The full spectrum of reduced species are formed in gasification. Many of these are incorporated into the quench water.	Dryer off gases may contain carbonyls.
① Coal Preparation	Same parameters and species as defined under "Refinery Operation," above.						
② Quenching and Cooling							
③ Fixed bed Catalyst Regeneration							
④ Sulfur Plant: Same as Claus Plant above.						Ⓛ $Ni(CO)_4$, NH_4CN, HCN	Ⓛ The existence of Arsine, Stibine, carbonyls and sulfides is probable.
⑤ Tar Separation							
Fertilizer Manufacturer	6.3% < 5μ, 12% < 10μ, 29% < 30μ, 34% < 40μ	0.7 to 4.0	ⓐ 16.5 (one unit)	201		Ⓖ NH_3, HF	Ⓖ Cyanides, Nitrosyls.

① Stream parameters are highly variable depending on process design, see text.

Process Identification	Effluent Characteristics From Predominant Process Operations					Reduced Species Present in Primary Effluents	
	Particulate Data						
	Size Distribution	gr/SCF	Flow Rate	Temperature ^{o}F	Moisture: Vol %	Cited from Literature	Probable Stream Based on Chemistry
Forest Products Industry							
ⓐ Kraft Pulp Mills						Ⓖ	Ⓖ
① recovery furnace	50-85% < 2μ	3-8 avg. 3-8	ⓐ 20-568 ⓑ 278-568	270-650 avg. 350	20-40	H_2S, Na_2S	COS FeS
② lime kiln	95% < 25μ	3-20	ⓐ 7-50	400-900	400-600 lbs/air dried ton	Ⓖ H_2S	Ⓖ COS, FeS, MgS, CaS
③ smelt dissolving	90% < 5μ	0.17-1.3	45 SCF/air dried ton	170-200	670 lbs/air dried ton	Ⓖ H_2S, Na_2S	
Primary Nonferrous Metals Industries							
ⓐ Copper						Ⓖ	Ⓛ
① roasting furnace	15% < 10μ	6-24	ⓐ 60-131	600-890		Cu_2S FeS	Liquid tailings from refining operations are likely to contain selenides, tellurides, and sulfides.
② electrolytic refining*						AsH_3	
ⓑ Lead							Ⓖ
① sinter machine	100% < 10μ	0.4-4.5	ⓐ 140 ⓑ 130	250-600		Ⓖ	PbS, ZnS
② Blast furnace	0.03 to 0.3	1-11	6-14	150-250		PbS	ZnS, CdS, COS
ⓒ Zinc						Ⓖ	
① roaster	14% < 5, 31% < 10 70% < 20	5-65	25-30	730-900		ZnS	
② sinter machine	100% < 10	0.4-4.5	140	320-700	Dew Point: 122-140		Ⓖ ZnS, PbS, CdS
ⓓ Aluminum	Submicron particulate		2000 to 4000 CFM/cell			Ⓖ	Ⓖ
① reduction cell		0.03-2.0				H_2S	COS, Na_2S, CaS, Al_2S_3 Electrode is concerned in the reduction process; considerable CO is formed. Metal carbonyls may therefore result.

*Process data for electrolytic refining is highly variable; literature does not site specific flow data.

present in the effluent of steel plant blast furnaces. The blast furnace effluent may also contain FeS, MgS, MnS, COS, CaS, $Fe(CO)_5$ and $Mn(CO)_{10}$. The sinter plant may also discharge COS and $Fe(CO)_5$.

Figure 2-1 shows the principle elements of an average steel plant blast furnace and sintering machine. Solid samples in the form of integrated composites may be obtained at the dust catcher and precipitator (points 1 and 3, respectively) of the furnace. The sintering machine has logical sampling points for integrated composite solid samples at the dust bins (point 1) and the cyclones (point 2).

Integrated composite liquid samples may be obtained from the gas washer (point 2) of the furnace. Particulate matter can be obtained by sampling the stack gas effluents of both processes. Fugitive gas emissions may be sampled from the surrounding area using a number of techniques discussed in Section 3.0.

2.2.2 Coke Ovens

Coke ovens are also integral parts of most steel plants, but their effluents have received significantly more attention than effluents from other portions of the plants. Amoung the reduced species which have been identified in the literature are: $Ni(CO)_4$; HCN; NH_3; H_2S; H_2; COS; CS_2, and NH_4CN. Other hydrides (e.g., AsH_3 and SbH_3), metal carbonyls, cyanides, and sulfides may be present in the gaseous and liquid effluent streams based on the process chemistry.

The gaseous effluents from coke ovens (see Figure 2-2 for a typical installation) may be sampled at the stack to obtain particulate matter and near the oven slots to determine fugitive emissions. An integrated composite liquid sample may be obtained at the sour quench water effluent (point 3 on Figure 2-2).

2.2.3 Coal-Fired Boilers

Although coal-fired boilers are not operated under reducing conditions, $Cr(CO)_6$ has been cited in the literature as a constituent of the gaseous effluent from the process. The presence of $Cr(CO)_6$ suggests the possible

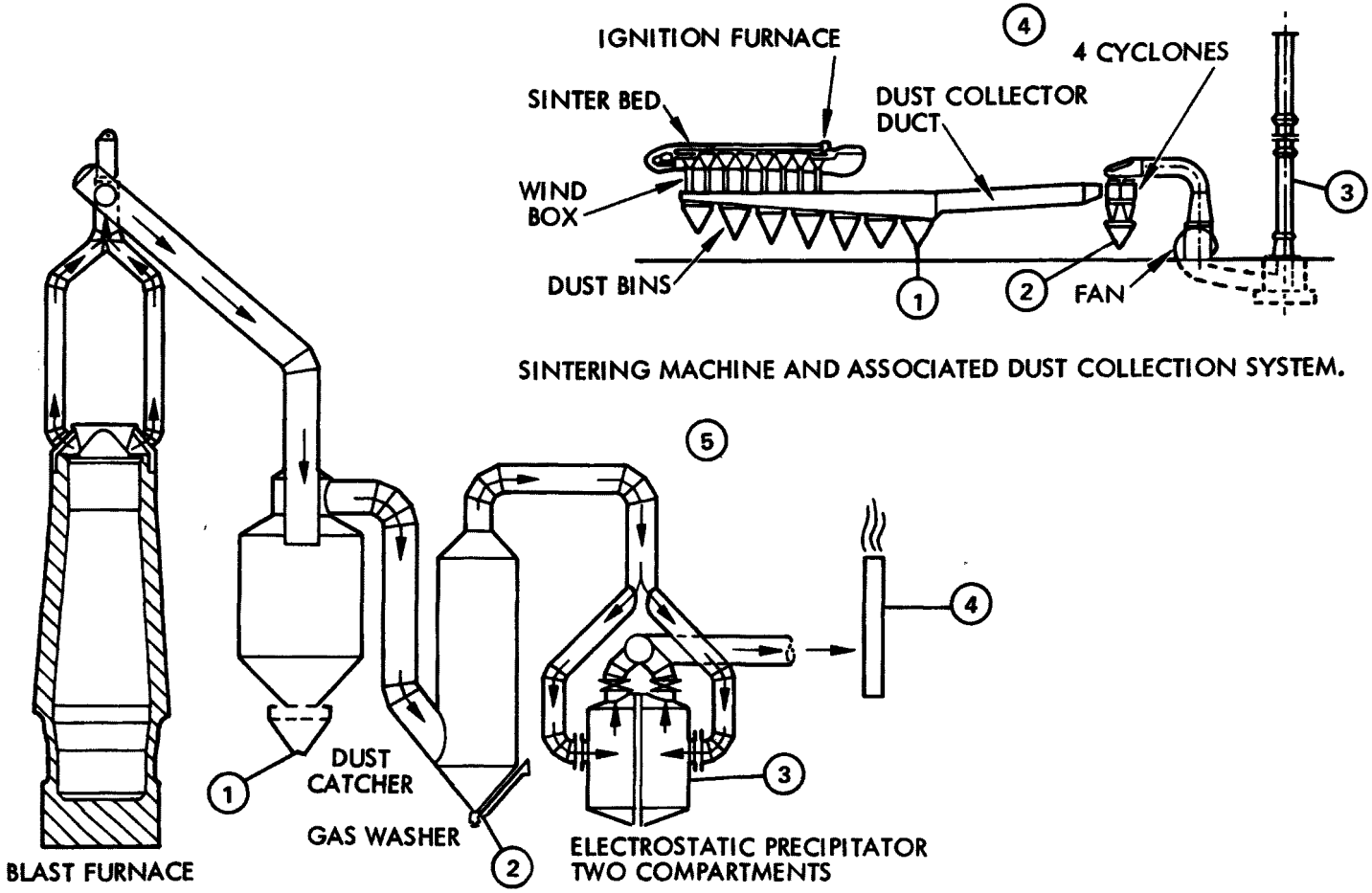


FIGURE 2-1A Blast Furnace and Sintering Machine With Associated Dust Collection System

POTENTIAL PROCESS SAMPLES

① SOLID: INTEGRATED COMPOSITE
② LIQUID: INTEGRATED COMPOSITE
③ SOLID: INTEGRATED COMPOSITE
④ GAS: PARTICULATE MATTER
⑤ GAS: FUGITIVE EMISSIONS

① SOLID: INTEGRATED COMPOSITE
② SOLID: INTEGRATED COMPOSITE
③ GAS: PARTICULATE MATTER
④ GAS: FUGITIVE EMISSIONS

PROCESS IDENTIFICATION	EFFLUENT CHARACTERISTICS FROM PREDOMINANT PROCESS OPERATIONS					REDUCED SPECIES PRESENT IN PRIMARY EFFLUENTS	
	PARTICULATE DATA						
	SIZE DISTRIBUTION	gr/SCF	FLOW RATE ①	TEMPERATURE °F	MOISTURE: VOL %	CITED FROM LITERATURE	PROBABLE STREAM BASED ON CHEMISTRY
1) STEEL PLANT						Ⓖ	Ⓖ
ⓐ BLAST FURNACE	15-90% < 74 μ	4-30,	ⓐ 40-140	390 AT THROAT	9.6	H_2	FeS, MgS, MnS
		7-10 AVG.	ⓑ 60-138	3000 AT FURNACE		H_2S	COS, CaS, $Fe(CO)_5$, $Mn(CO)_{10}$
ⓑ SINTER PLANT							Ⓖ
① WINDBOX:	14-45% < 40 μ	0.2-3.2	ⓐ 30-460	100-400	2-10		COS, $Fe(CO)_5$
	9-30% < 20 μ		ⓑ 148-230				
	4-19% < 10 μ						Ⓖ
	1-10% < 5 μ	1-5	ⓐ 0.03-0.2	100-300			COS, $Fe(CO)_5$
② DISCHARGE END:	80% < 100 μ						
	10% < 10 μ						

FIGURE 2-1B Blast Furnace and Sintering Machine with Associated Dust Collection System

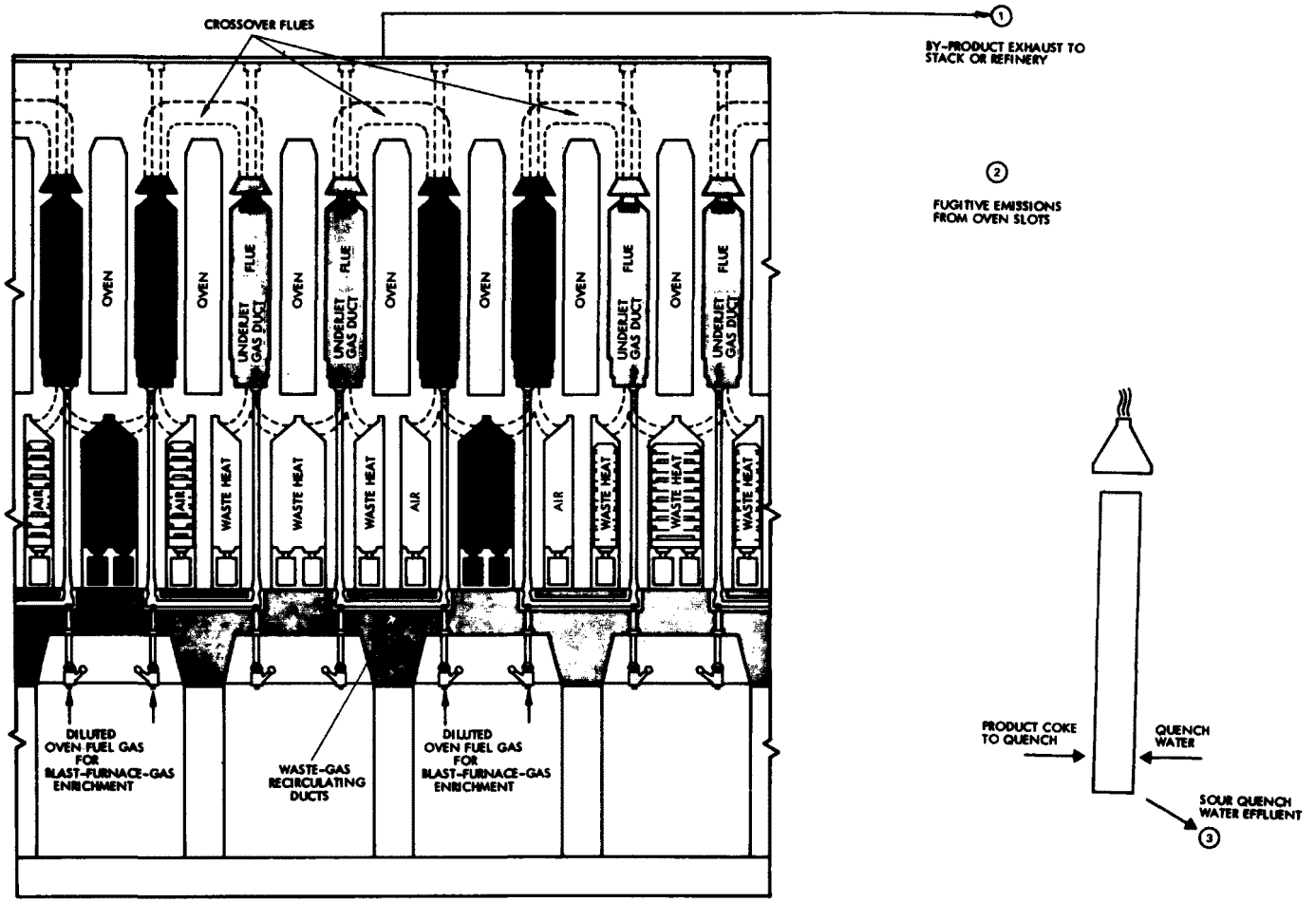


FIGURE 2-2A Coke Oven Battery

PROCESS IDENTIFICATION	EFFLUENT CHARACTERISTICS FROM PREDOMINANT PROCESS OPERATIONS					REDUCED SPECIES PRESENT IN PRIMARY EFFLUENTS	
	PARTICULATE DATA						
	SIZE DISTRIBUTION	gr/SCF	FLOW RATE	TEMPERATURE °F	MOISTURE: VOL %	CITED FROM LITERATURE	PROBABLE STREAM BASED ON CHEMISTRY
(b) COKE OVENS							
(1) OVEN OFF GAS	HIGHLY VARIABLE	1-15	2.1 M FT^3 PER CHARGE	≤ 1832	VARIABLE DEPENDING ON POINT IN COKING CYCLE	(G) $Ni(CO)_4$, HCN, NH_3 H_2S, H_2, COS, CS_2, NH_4CN	(G) AsH_3, SbH_3 THE FORMATION OF A VARIETY OF HYDRIDES, CARBONYL, AND METAL SULFIDES IS POSSIBLE.
(2) QUENCH TOWER	95-97% >47 μ	0.05-0.1	900 M FT^3 PER QUENCH	140-150	EFFLUENT CONSISTS PRIMARILY OF STEAM	(G) (L) $Ni(CO)_4$, HCN, H_2, NH_3, NH_4CN, COS, CS_2	(G) (L) THE FORMATION OF A VARIETY OF HYDRIDES, CARBONYLS, AND METAL SULFIDES IS POSSIBLE.
(3) SOUR QUENCH WATER	NOT APPLICABLE		WATER USUALLY SLUICED; FLOW VARIABLE AND CYCLIC			(L) CYANIDE AND AMMONIA SPECIES ARE CITED IN THE LITERATURE. DISTINCT COMPOUNDS ARE NOT IDENTIFIED.	(L) METAL SULFIDES, CYANIDES, SULFUR CYANIDES, AND REDUCED AMMONIA SPECIES.

POTENTIAL PROCESS SAMPLES

(1) GAS: PARTICULATE MATTER

(2) GAS: FUGITIVE EMISSIONS

(3) LIQUID: INTEGRATED COMPOSITE

FIGURE 2-2B Coke Oven Battery

formation of other metal carbonyls under similar conditions.

The metal carbonyls cited in the literature may be sought in the fugitive emissions from the boilers and by sampling the stack gases. The inherent instability of metal carbonyls will make sampling with a goal of subsequent compound identification very difficult if not impossible.

2.2.4 Refinery Operations

Many of the operations commonly performed during the refining of crude oil and other associated processes are conducted under reducing conditions. The nature of the effluents from these operations have been the subject of several investigations. A partial list of the species reported (see Table 2-1 for a more complete list of species and specific effluent streams) are: H_2S; COS; CS_2; NH_3; HCN; $Ni(CO)_4$ and $[Co(CO)_4]_2$. Other carbonyls, cyanides, sulfides and hydrides are suspected in the gaseous and liquid effluent streams.

Time integrated gas samples may be taken at a number of points in a typical refinery complex (Figure 2-3) to trap gaseous reduced species. The hydrocracking and catalytic cracking units (points 1 and 2, respectively) are typical locations, as are the asphalt still (point 5) and the sulfur plant (point 6). In some instances specific on-line measurement techniques may be useful. On-line methods should be employed whenever possible, since the high reactivity of many of the reduced inorganic species of interest may lead to erroneous results if conventional integrated bag or metal container samples are used or if analysis is delayed. Also the on-line method provides process variation and up-set information not normally observed during sampling visits.

Particulate matter samples may be obtained from the gas streams of the coker (point 3) and catalytic reforming unit (point 4). Fugitive emisions can only be determined by a sampling matrix designed for each individual plant, not generalized to the industry.

2.2.5 Coal Conversion

A number of coal liquifaction and gasification processes are now in

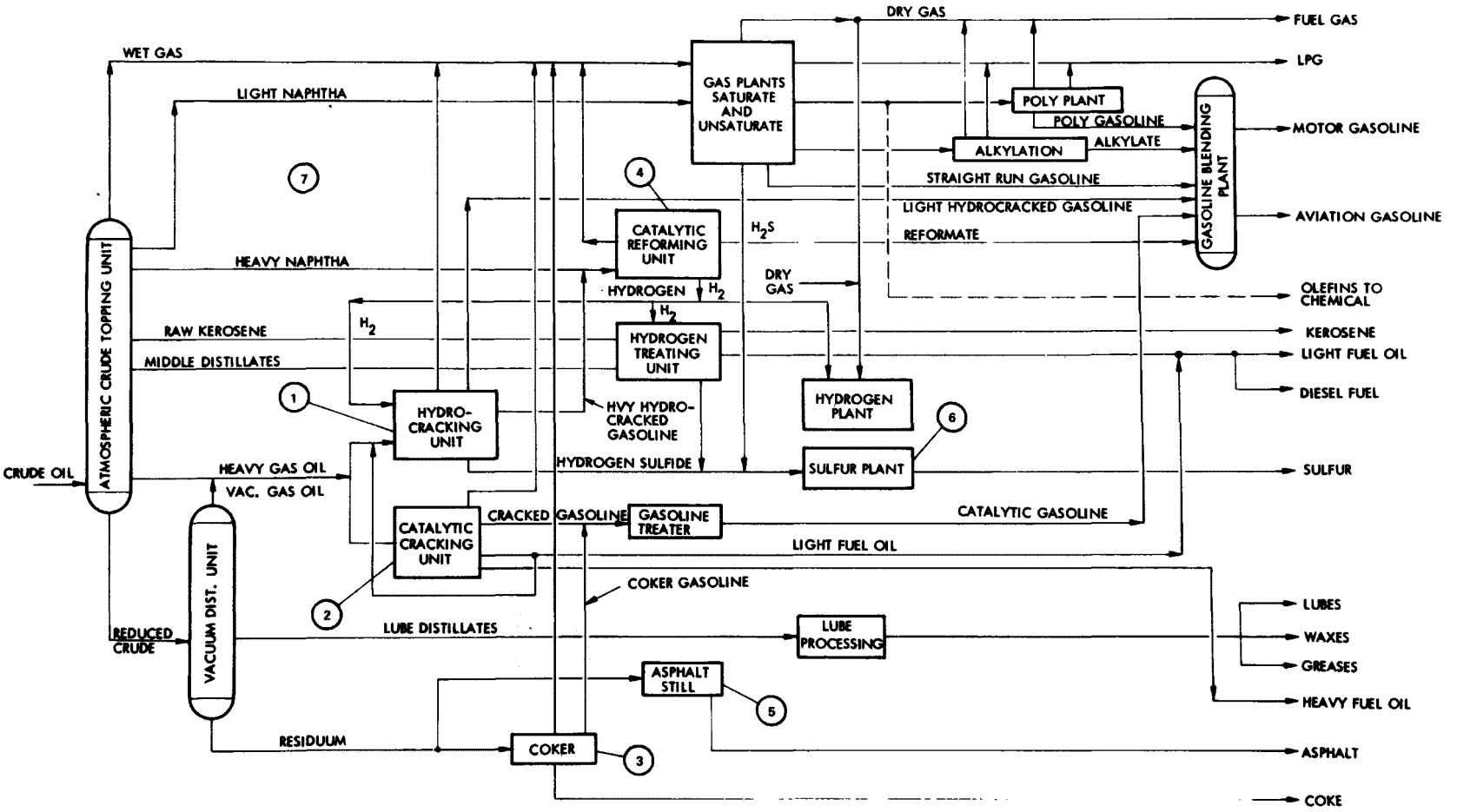


FIGURE 2-3A Processing Plant for Typical Complete Refinery

POTENTIAL PROCESS SAMPLES

① GAS: TIME INTEGRATED
② GAS: TIME INTEGRATED
③ GAS: PARTICULATE MATTER
④ GAS: PARTICULATE MATTER [FROM CATALYST REGENERATION]
⑤ GAS: TIME INTEGRATED
⑥ GAS: TIME INTEGRATED
⑦ GAS: FUGITIVE EMISSIONS [PLANT MATRIX]

	EFFLUENT CHARACTERISTICS FROM PREDOMINANT PROCESS OPERATIONS					REDUCED SPECIES PRESENT IN PRIMARY EFFLUENTS	
	PARTICULATE DATA						
PROCESS IDENTIFICATION	SIZE DISTRIBUTION	gr/SCF	FLOW RATE	TEMPERATURE °F	MOISTURE: VOL %	CITED FROM LITERATURE	PROBABLE STREAM BASED ON CHEMISTRY
REFINERY OPERATIONS ⓐ CLAUS PLANT TAIL GAS ⓑ FIXED BED CATALYST REGENERATION ⓒ MOVING BED CATALYST REGENERATION ⓓ FLUID COKER OFF-GAS				FIXED AND MOVING BED REGENERABLE CATALYSTS FUNCTION AT ABOUT 850 TO 1000 °F AT 300 TO 700 PSIG		Ⓖ H_2S, COS, CS_2, NH_3, HCN H_2S, COS, CS_2, $Ni(CO)_4$ $[Co(CO)_4]_2$ H_2S, COS, CS_2, NH_3, $Ni(CO)_4$, HCN H_2S, COS, CS_2, NH_3, RCN, $Ni(CO)_4$	Ⓖ Ⓛ SPENT CHEMICALS FROM ACID GAS AMINE SOLUTION REGENERATION = CARBONYLS, CYANIDES, SULFIDES. $Mo(CO)_6$; THE FORMATION OF VARIOUS METAL SULFIDES, HYDRIDES AND CARBONYLS PROBABLE. METAL SULFIDES AND CARBONYLS PROBABLE.

FIGURE 2-3B Processing Plant for Typical Complete Refinery

various stages of development. The chemistry and operating condition of the various processes differ significantly, however all of the conversion processes involve operations which take place under reducing conditions. A wide spectrum of reduced species, both organic and inorganic, can be expected in the gaseous, liquid and solid effluents of these processes. Table 2-1 lists some specific examples, however the identities and relative quantities of the reduced inorganic species emitted from a process will be site specific.

The Lurgi process was chosen as an example to illustrate the location of potential sampling points in a coal gasification complex (Figure 2-4). Integrated composite solid samples may be taken from the ash produced in the gasifier (points 3 and 2). Time integrated gas samples should be obtained from the aqueous streams produced in the purification and treatment operations. It is also important to trap particulate matter present in the gaseous effluent from the coal preparation (point 1) and catalyst regeneration (point 11) operations. A carefully designed sampling matrix should be implemented to determine fugitive emmisions.

Figure 2-5 shows the principle operations of a typical coal liquifaction complex. A sampling matrix to determine fugitive emissions is appropriate, as is the obtaining of integrated composite liquid samples from all of the effluent aqueous streams. Of particular importance is an integrated sample of spent scrubber solution (point 6). Particulate matter in the gas streams from the coal preparation, catalyst regeneration and preheater units should be sampled. Gaseous effluents should be determined by obtaining a time integrated gas sample from the stack of the gas treatment units (point 5).

2.2.6 Fertilizer Manufacturing

Ammonium nitrate is the principal, commercially produced, synthetic fertilizer. Ammonia and hydrogen fluoride have been reported as present in the effluents from nitrate fertilizer manufacturing. The conditions normally employed in the production of ammonium nitrate may also result in the formation of cyanides and nitrosyls.

Nitrate fertilizer plants (Figure 2-6) should be sampled for fugitive

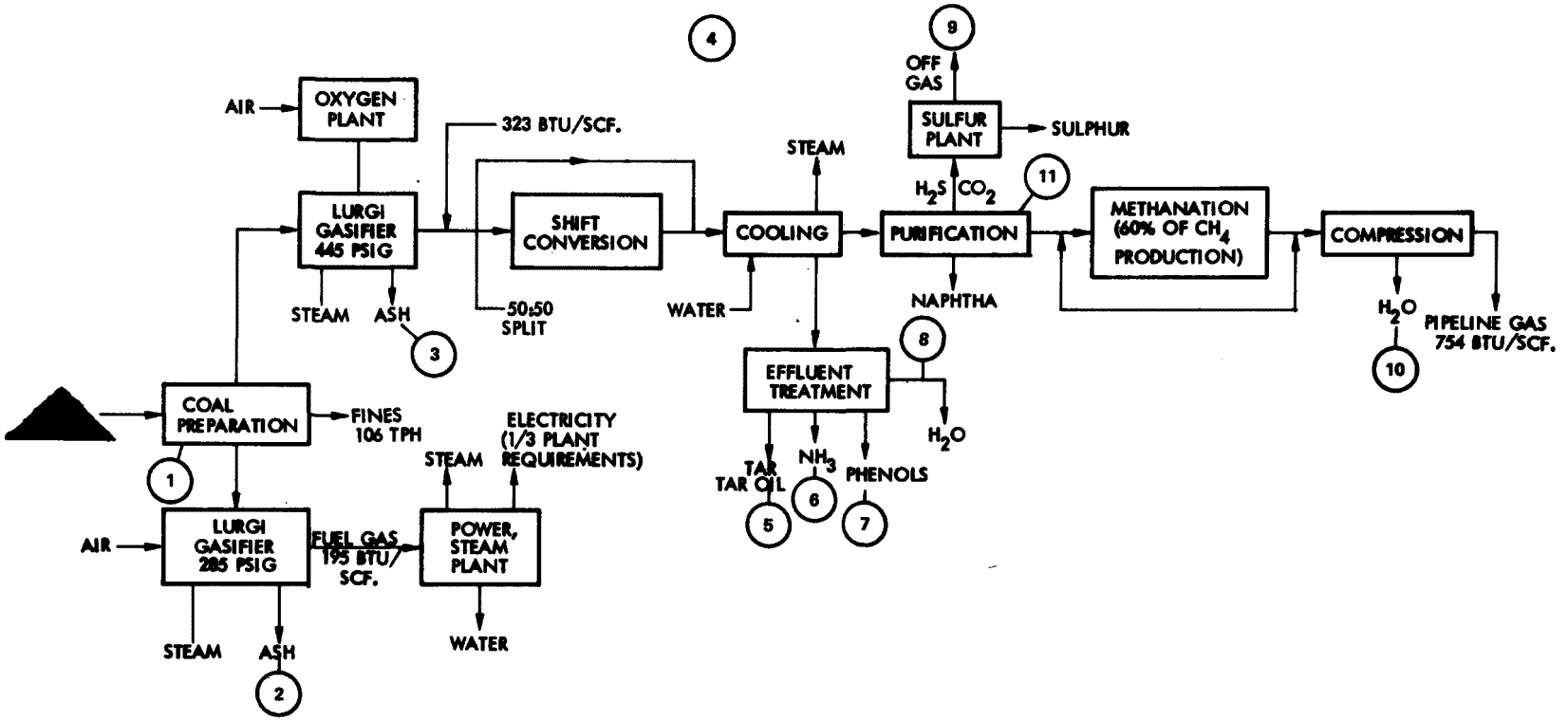


FIGURE 2-4A Simplified Gasification Complex (Lurgi)

PROCESS IDENTIFICATION	EFFLUENT CHARACTERISTICS FROM PREDOMINANT PROCESS OPERATIONS					REDUCED SPECIES PRESENT IN PRIMARY EFFLUENTS	
	PARTICULATE DATA						
	SIZE DISTRIBUTION	gr/SCF	FLOW RATE	TEMPERATURE °F	MOISTURE: VOL %	CITED FROM LITERATURE	PROBABLE STREAM BASED ON CHEMISTRY
COAL CONVERSION (1) (o) GASIFICATION AND LIQUEFACTION OPERATIONS (1) COAL PREPARATION (2) QUENCHING AND COOLING (3) FIXED BED CATALYST: SAME PARAMETERS AND SPECIES AS DEFINED UNDER "REFINERY OPERATION," ABOVE. REGENERATION (4) SULFUR PLANT: SAME AS CLAUS PLANT ABOVE (5) TAR SEPARATION						SULFIDES IN RINSE SOLUTION AND PARTICULATE- THE FULL SPECTRUM OF REDUCED SPECIES ARE FORMED IN GASIFICATION. MANY OF THESE ARE INCORPORATED INTO THE QUENCH WATER. (L) $Ni(CO)_4$, NH_4CN, HCN	DRYER OFF GASES MAY CONTAIN CARBONYLS. (L) THE EXISTENCE OF ARSINE, STIBINE, CARBONYLS AND SULFIDES IS PROBABLE.

(1) STREAM PARAMETERS ARE HIGHLY VARIABLE DEPENDING ON PROCESS DESIGN, SEE TEXT.

POTENTIAL PROCESS SAMPLES

(1) GAS: PARTICULATE MATTER
(2) SOLID: INTEGRATED COMPOSITE
(3) SOLID: INTEGRATED COMPOSITE
(4) GAS: FUGITIVE EMISSIONS MATRIX
(5) GAS: TIME INTEGRATED
(6) GAS: TIME INTEGRATED
(7) GAS: TIME INTEGRATED
(8) LIQUID: INTEGRATED COMPOSITE
(9) GAS: TIME INTEGRATED
(10) LIQUID: INTEGRATED COMPOSITE
(11) GAS: PARTICULATE MATTER [CATALYST REGENERATION]

FIGURE 2-4B Simplified Gasification Complex (Lurgi)

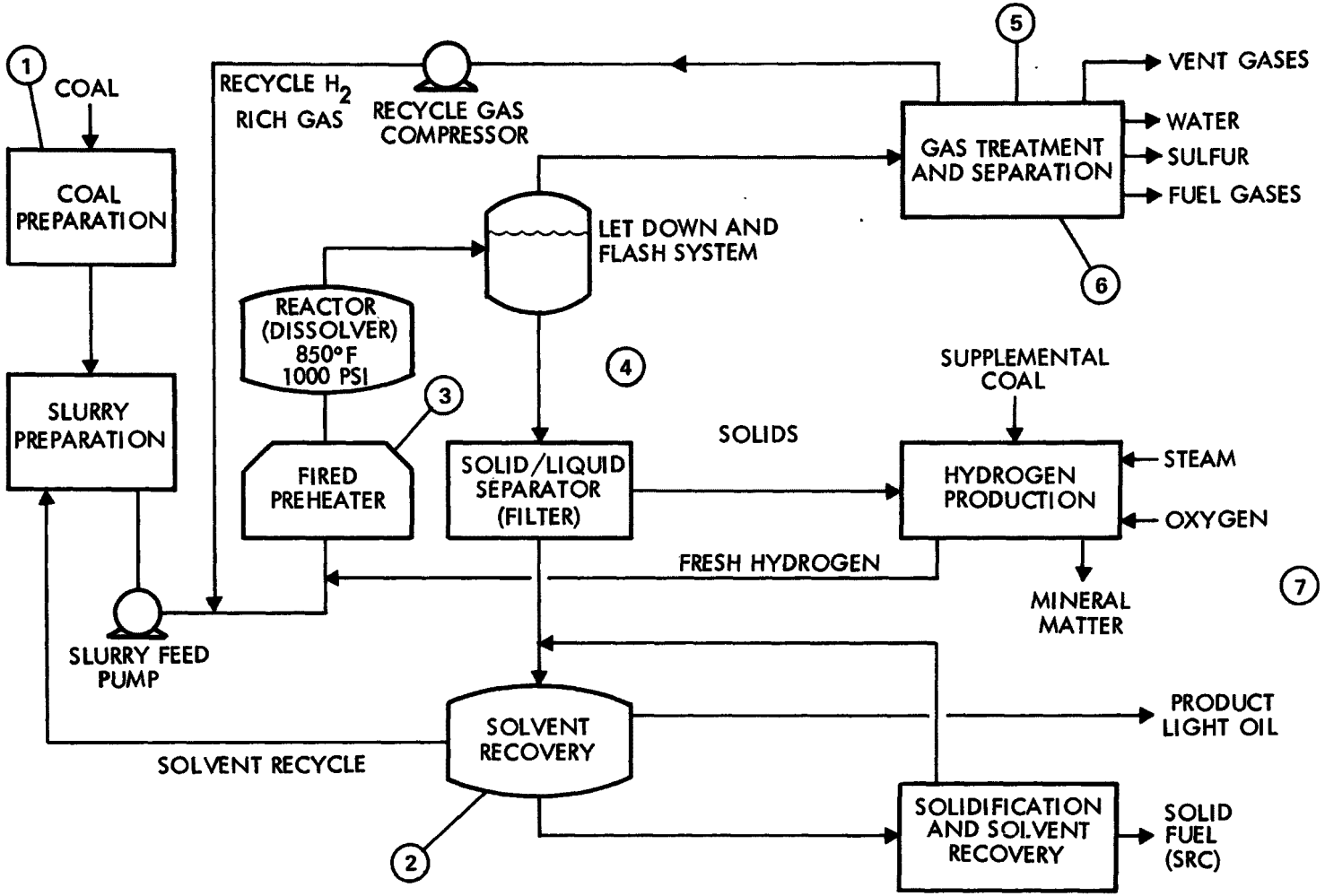


FIGURE 2-5A Simplified Liquifaction Complex (SRC)

POTENTIAL PROCESS SAMPLES

(1) GAS: PARTICULATE MATTER

(2) GAS: PARTICULATE [CATALYST REGENERATION]

(3) GAS: PARTICULATE MATTER

(4) LIQUID: VARIOUS SOUR WATER STREAMS; TIME INT.

(5) GAS: TIME INTEGRATED

(6) LIQUID: INTEGRATED COMPOSITE [SPENT SCRUBBER SOLUTION]

(7) GAS: FUGITIVE EMISSIONS MATRIX

PROCESS IDENTIFICATION	EFFLUENT CHARACTERISTICS FROM PREDOMINANT PROCESS OPERATIONS					REDUCED SPECIES PRESENT IN PRIMARY EFFLUENTS	
	PARTICULATE DATA						
	SIZE DISTRIBUTION	gr/SCF	FLOW RATE	TEMPERATURE °F	MOISTURE: VOL %	CITED FROM LITERATURE	PROBABLE STREAM BASED ON CHEMISTRY
COAL CONVERSION (1)							
(a) GASIFICATION AND LIQUEFACTION OPERATIONS						SULFIDES IN RINSE SOLUTION AND PARTICULATE. THE FULL SPECTRUM OF REDUCED SPECIES ARE FORMED IN GASIFICATION. MANY OF THESE ARE INCORPORATED INTO THE QUENCH WATER.	DRYER OFF GASES MAY CONTAIN CARBONYLS.
(1) COAL PREPARATION							
(2) QUENCHING AND COOLING							
(3) FIXED BED CATALYST REGENERATION	SAME PARAMETERS AND SPECIES AS DEFINED UNDER "REFINERY OPERATION," ABOVE.						
(4) SULFUR PLANT: SAME AS CLAUS PLANT ABOVE.						(L) $Ni(CO)_4$, NH_4CN, HCN	(L) THE EXISTENCE OF ARSINE, STIBINE, CARBONYLS AND SULFIDES IS PROBABLE.
(5) TAR SEPARATION							

(1) STREAM PARAMETERS ARE HIGHLY VARIABLE DEPENDING ON PROCESS DESIGN, SEE TEXT.

FIGURE 2-5B Simplified Liquifaction Complex (SRC)

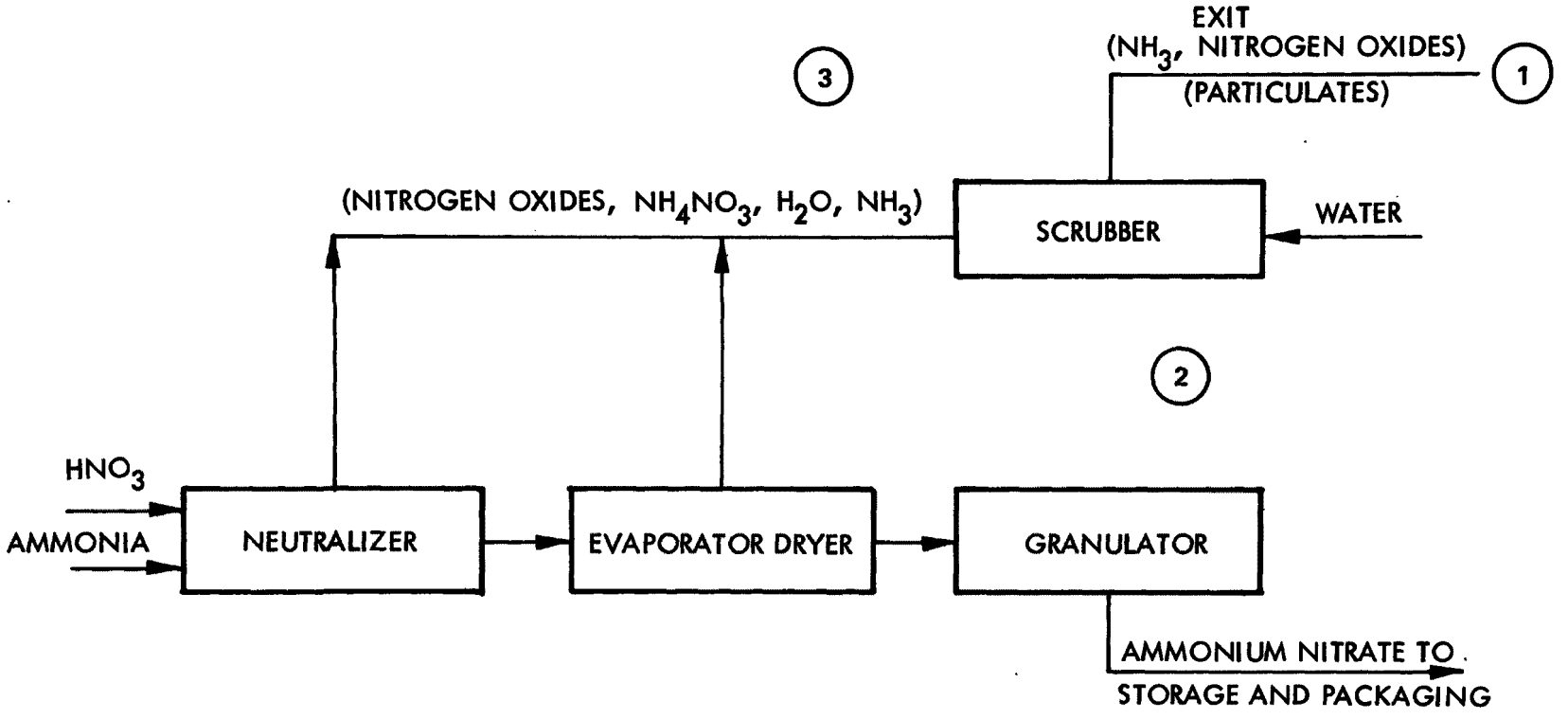


FIGURE 2-6A

Flow Diagram of The Process for Manufacture of Ammonium Nitrate

POTENTIAL PROCESS SAMPLES

① GAS: PARTICULATE MATTER
② LIQUID: INTEGRATED COMPOSITE
③ GAS: FUGITIVE EMISSIONS [PLANT MATRIX]

	EFFLUENT CHARACTERISTICS FROM PREDOMINANT PROCESS OPERATIONS					REDUCED SPECIES PRESENT IN PRIMARY EFFLUENTS	
	PARTICULATE DATA						
PROCESS IDENTIFICATION	SIZE DISTRIBUTION	gr/SCF	FLOW RATE	TEMPERATURE °F	MOISTURE: VOL %	CITED FROM LITERATURE	PROBABLE STREAM BASED ON CHEMISTRY
FERTILIZER MANUFACTURER	6.3% < 5μ, 12% < 10μ, 29% < 30μ, 34% < 40μ,	0.7 TO 4.0	① 16.5 (ONE UNIT)	201		Ⓖ NH_3, HF	Ⓖ CYANIDES, NITROSYLS

FIGURE 2-6B

Flow Diagram of The Process for Manufacture of Ammonium Nitrate

gaseous emissions. The gaseous stream emanation from the scrubber (point 1) should be sampled to obtain particulate matter and an integrated composite liquid sample should be obtained from the aqueous effluent streams.

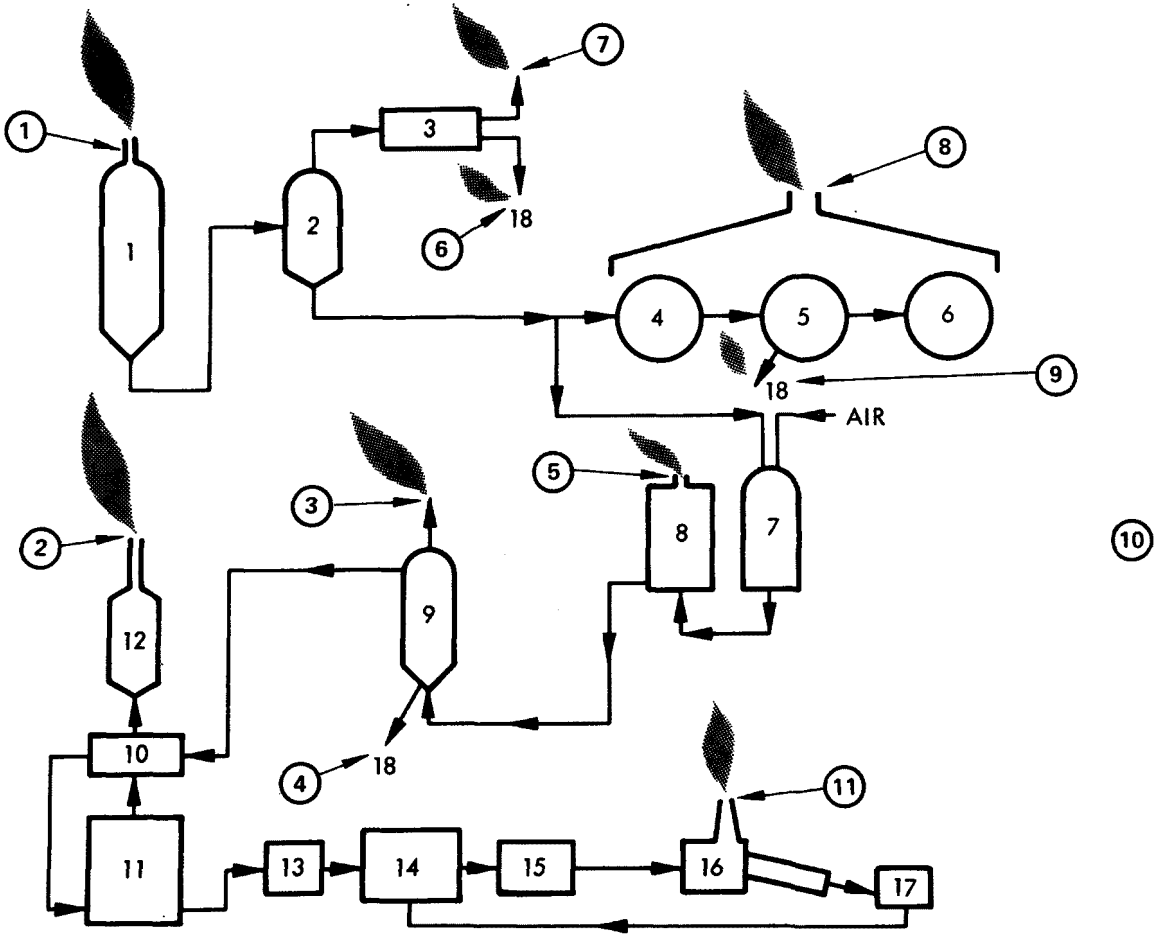
2.2.7 Forest Products

Paper is the major non-wood product of the forest products industries and the Kraft process (Figure 2-7) is employed in the production of a significant portion of that product. Kraft pulp mills produce a number of reduced species of interest, even though many of the operations involved are actually oxidation. H_2S and Na_2S are the two reduced inorganic species which have been repeatedly cited in the literature as being present in the effluent of Kraft mills. It is also probable that COS, FeS, MgS, and CaS are produced in the process and are present in the effluent.

Time integrated gas samples may be taken at the digester (point 1), blow heat recovery unit (point 7), form tank (point 5), multiple-effect evaporator (point 3) and the lime kiln (point 11). Fugitive gas emissions may be determined by a plant matrix and at some specific sources subject to equipment leaks (e.g., point 8). Particulate samples from the gas stream emanating from the electrostatic precipitator (point 2) should be of interest. Integrated composite liquid samples may be taken from the aqueous streams coming from the multiple-effect evaporator (point 4), the blow tank heat recovery unit (point 6) and the screens (point 9).

2.2.8 Primary Nonferrous Metals

The primary nonferrous metals group includes copper, lead, zinc, and aluminum. There is considerable variation in the processes used to make each of these metals, and in some instances particularly in aluminium there are new processes under development which differ significantly from those currently in vogue. However, the simplified flow diagrams show in Figures 2-8 to 2-11 represent typical plants for which information is now available.



SIMPLIFIED KRAFT MILL FLOW DIAGRAM. 1, DIGESTER; 2, BLOW TANK; 3, BLOW HEAT RECOVERY; 4, WASHERS; 5, SCREENS; 6, DRYERS; 7, OXIDATION TOWER; 8, FORM TANK; 9, MULTIPLE-EFFECT EVAPORATOR; 10, DIRECT EVAPORATOR; 11, RECOVERY FURNACE; 12, ELECTROSTATIC PRECIPITATOR; 13, DISSOLVER; 14, CAUSTICIZER; 15, MUD FILTER; 16, LIME KILN; 17, SLAKER; 18, SEWER.

FIGURE 2-7A Simplified Kraft Mill Flow Diagram

POTENTIAL PROCESS SAMPLES

① GAS: TIME INTEGRATED
② GAS: PARTICULATE MATTER
③ GAS: TIME INTEGRATED
④ LIQUID: INTEGRATED COMPOSITE
⑤ GAS: TIME INTEGRATED
⑥ LIQUID: INTEGRATED COMPOSITE
⑦ GAS: TIME INTEGRATED
⑧ GAS: FUGITIVE EMISSIONS [SPECIFIC SOURCE]
⑨ LIQUID: INTEGRATED COMPOSITE
⑩ GAS: FUGITIVE EMISSIONS [PLANT MATRIX]
⑪ GAS: TIME INTEGRATED

PROCESS IDENTIFICATION	EFFLUENT CHARACTERISTICS FROM PREDOMINANT PROCESS OPERATIONS					REDUCED SPECIES PRESENT IN PRIMARY EFFLUENTS	
	PARTICULATE DATA						
	SIZE DISTRIBUTION	gr/SCF	FLOW RATE	TEMPERATURE °F	MOISTURE: VOL %	CITED FROM LITERATURE	PROBABLE STREAM BASED ON CHEMISTRY
FOREST PRODUCTS INDUSTRY							
ⓐ KRAFT PULP MILLS						Ⓖ	Ⓖ
① RECOVERY FURNACE	50-85% < 2 μ	3-8 AVG. 3-8	ⓐ 20-568 ⓑ 278-568	270-650 AVG. 350	20-40	H_2S, Na_2S	COS FeS
② LIME KILN	95% < 25 μ	3-20	ⓐ 7-50	400-900	400-600 LBS/AIR DRIED TON	Ⓖ H_2S	Ⓖ COS, FeS, MgS, CaS
③ SMELT DISSOLVING	90% < 5 μ	0.17-1.3	45 SCF/AIR DRIED TON	170-200	670 LBS/AIR DRIED TON	Ⓖ H_2S, Na_2S	

FIGURE 2-7B Simplified Kraft Mill Flow Diagram

Copper --

The literature identified Cu_2S and FeS as present in the effluent from copper roasting furnaces and AsH_3 as emanating from the electrolytic refining unit. It is also likely that liquid tailings from refining operations will contain selenides, tellurides and sulfides.

Appropriate liquid sampling points at a copper smelting plant (Figure 2-8) are the quench tank (point 3), the scrubber (point 4) and the refining operations (point 7). Integrated gas samples should also be taken at the refining operation (point 7) and at the acid plant (point 6). A plant sampling matrix to ascertain the level of fugitive emissions should also be performed and a sample of particulate matter in the gas stream from the electrostatic precipitators (points 1 and 5) should be obtained.

Lead --

Lead sulfide has been reported to be present in the gaseous effluent from the lead blast furnace (Figure 2-9). In addition, this stream may also contain ZnS, CdS and COS. The sinter machine is also likely to be a source of PbS and ZnS.

Points 1,2,3 and 4 are suggested for sampling particulate contained in gas streams. A plant sampling matrix to determine fugitive gaseous emissions may also be performed.

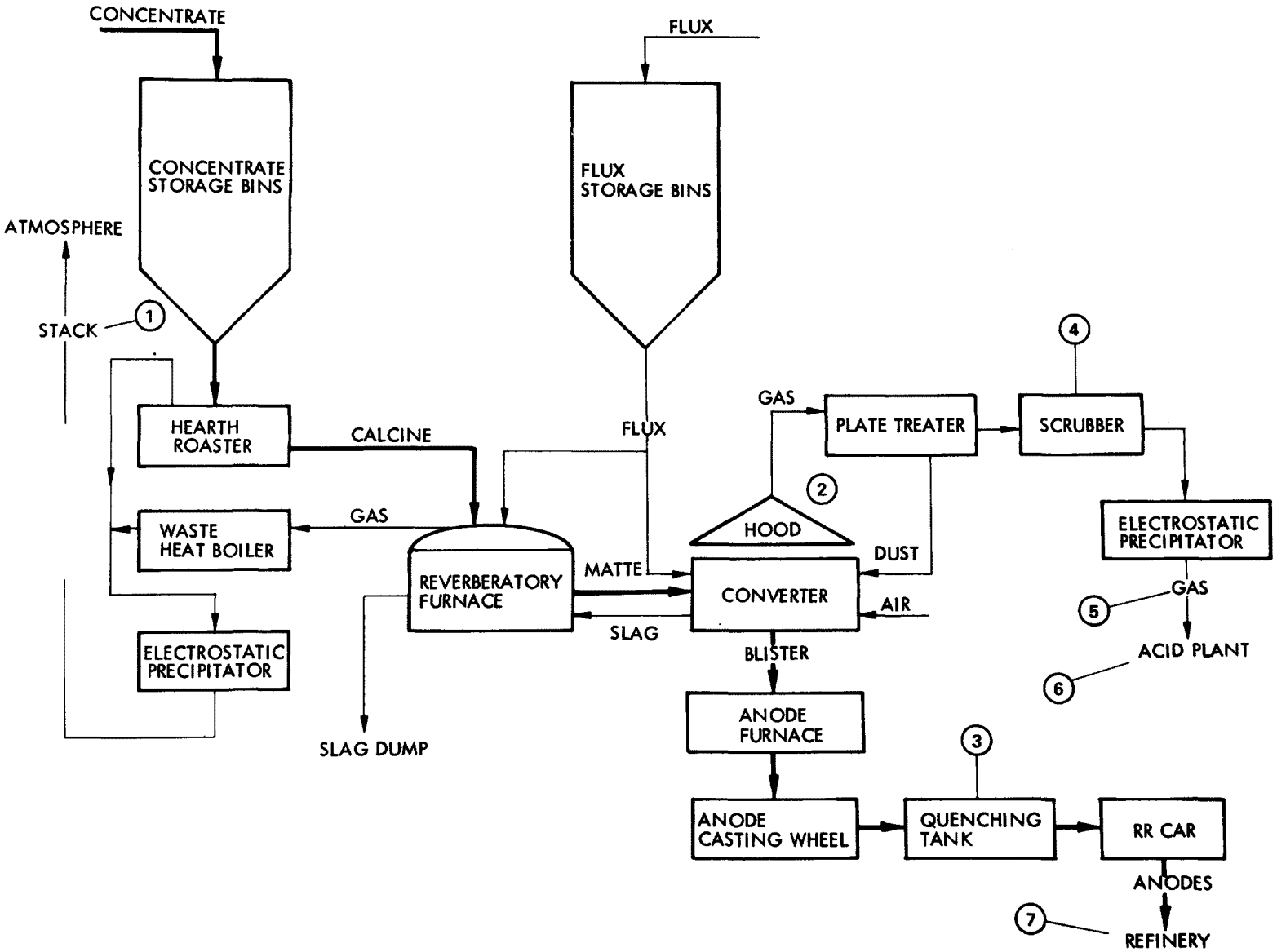
Zinc --

Zinc sulfide has been found in the effluent from the roasting operation (Figure 2-10). ZnS along with PbS and CdS are likely to be found in the sinter machine effluent also. Integrated composite solid samples may be obtained from Points 2 and 4. The stacks from the dust collection system (point 1) and roasting furnace (point 3) operations may be sampled for particulate.

Aluminium --

Hydrogen sulfide is the only reduced inorganic compound identified in literature as present in the effluent from aluminium refining operations. It is also likely based on the chemistry of the process that COS, Na_2S, CaS, Al_2S_3, and various metal carbonyls will be present. Potentially useful areas to obtain process samples (Figure 2-11) are the potline

(time integrated gas sample and fugitive emissions) and the scrubbers (particulate matter from the exhaust and an integrated composite liquid sample).



*PROCESS DATA FOR ELECTROLYTIC REFINING IS HIGHLY VARIABLE; LITERATURE DOES NOT SITE SPECIFIC FLOW DATA

FIGURE 2-8A Copper Smelting - Simplified Flow Diagram

POTENTIAL PROCESS SAMPLES

① GAS: PARTICULATE MATTER
② GAS: FUGITIVE EMISSIONS [SPECIFIC SOURCE]
③ LIQUID: INTEGRATED COMPOSITE
④ LIQUID: INTEGRATED COMPOSITE
⑤ GAS: PARTICULATE MATTER
⑥ GAS: TIME INTEGRATED
⑦ ⓐ LIQUID: INTEGRATED COMPOSITE
ⓑ GAS: TIME INTEGRATED

PROCESS IDENTIFICATION	EFFLUENT CHARACTERISTICS FROM PREDOMINANT PROCESS OPERATIONS					REDUCED SPECIES PRESENT IN PRIMARY EFFLUENTS	
	PARTICULATE DATA					CITED FROM LITERATURE	PROBABLE STREAM BASED ON CHEMISTRY
	SIZE DISTRIBUTION	gr/SCF	FLOW RATE	TEMPERATURE °F	MOISTURE: VOL %		
PRIMARY NONFERROUS METALS INDUSTRIES							
ⓐ COPPER						Ⓖ	Ⓛ
① ROASTING FURNACE	15% < 10	6-24	ⓐ 60 - 131	600 - 890		Cu_2S FeS	LIQUID TAILINGS FROM REFINING OPERATIONS ARE LIKELY TO CONTAIN SELENIDES, TELLURIDES, AND SULFIDES.
② ELECTROLYTIC REFINING*						AsH_3	

FIGURE 2-8B Copper Smelting - Simplified Flow Diagram

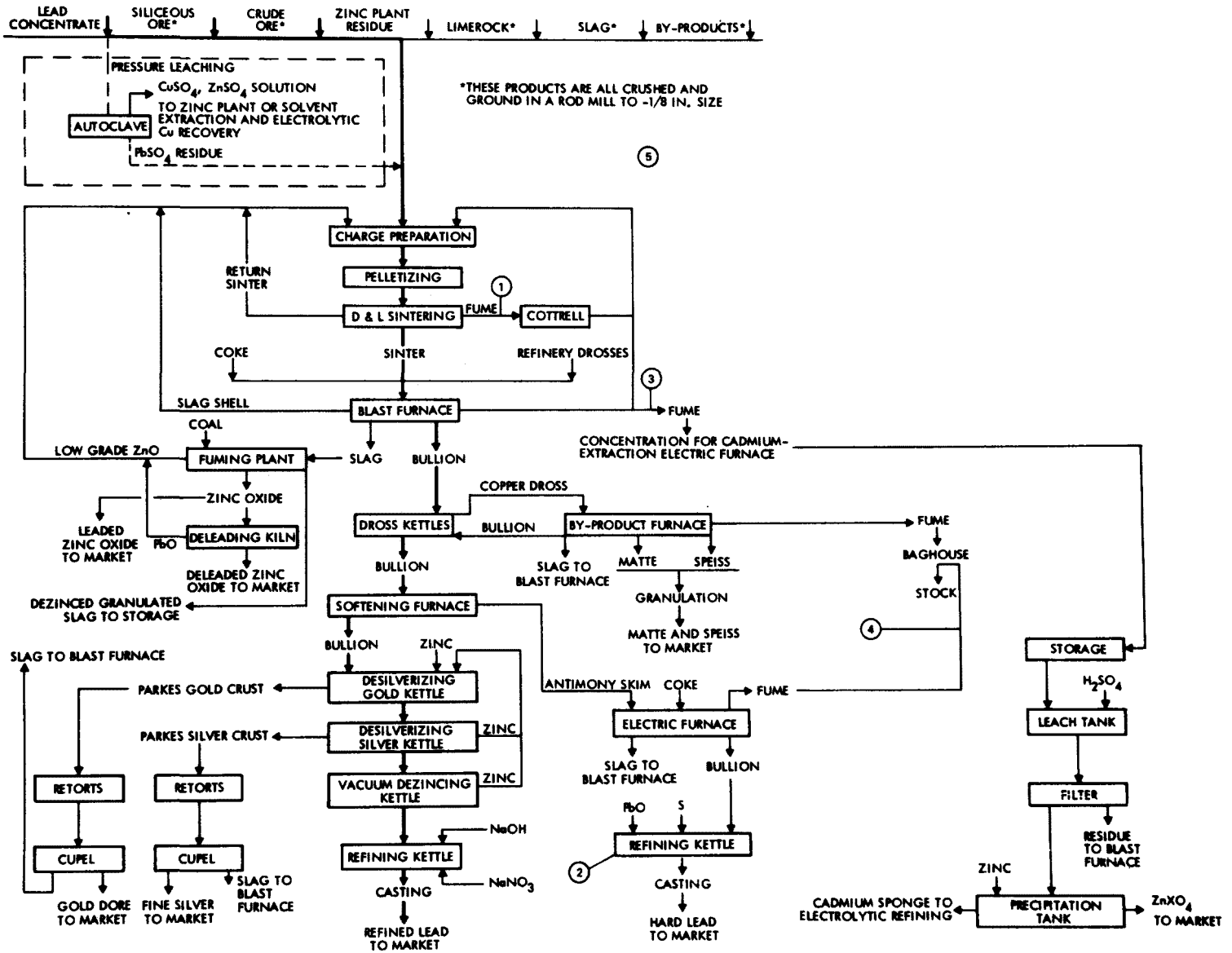


FIGURE 2-9A Typical Flowsheet of Pyrometallurgical Lead Smelting

POTENTIAL PROCESS SAMPLES

(1) GAS: PARTICULATE MATTER

(2) GAS: PARTICULATE MATTER

(3) GAS: PARTICULATE MATTER

(4) GAS: PARTICULATE MATTER

(5) GAS: FUGITIVE EMISSIONS [PLANT MATRIX]

PROCESS IDENTIFICATION	EFFLUENT CHARACTERISTICS FROM PREDOMINANT PROCESS OPERATIONS					REDUCED SPECIES PRESENT IN PRIMARY EFFLUENTS	
	PARTICULATE DATA						
	SIZE DISTRIBUTION	gr/SCF	FLOW RATE	TEMPERATURE °F	MOISTURE: VOL %	CITED FROM LITERATURE	PROBABLE STREAM BASED ON CHEMISTRY
(b) LEAD							(G)
(1) SINTER MACHINE	100% < 10μ	0.4-4.5	(a) 140 (b) 130	250-600		(G)	PbS, ZnS
(2) BLAST FURNACE	0.03 TO 0.3	1-11	6-14	150-250		PbS	ZnS, CdS, COS

FIGURE 2-9B Typical Flowsheet of Pyrometallurgical Lead Smelting

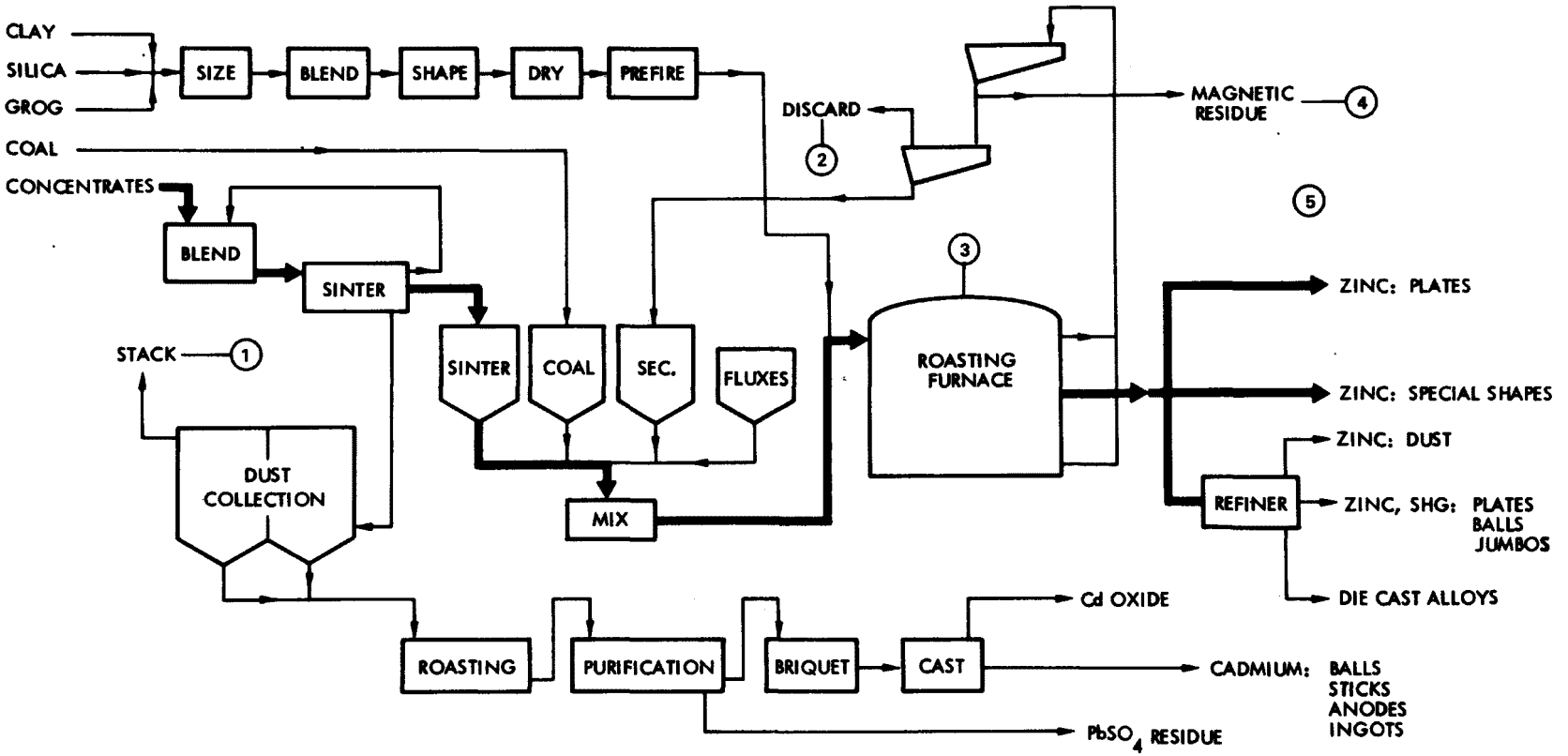


FIGURE 2-10A Zinc Smelting Flow Diagram

POTENTIAL PROCESS SAMPLES

① GAS: PARTICULATE MATTER
② SOLID: INTEGRATED COMPOSITE
③ GAS: PARTICULATE MATTER
④ SOLID: INTEGRATED COMPOSITE
⑤ GAS: FUGITIVE EMISSIONS [PLANT MATRIX]

PROCESS IDENTIFICATION	EFFLUENT CHARACTERISTICS FROM PREDOMINANT PROCESS OPERATIONS					REDUCED SPECIES PRESENT IN PRIMARY EFFLUENTS	
	PARTICULATE DATA						
	SIZE DISTRIBUTION	gr/SCF	FLOW RATE	TEMPERATURE °F	MOISTURE: VOL %	CITED FROM LITERATURE	PROBABLE STREAM BASED ON CHEMISTRY
ⓒ ZINC							
① ROASTER	14% < 5 31% < 10 70% < 20	5-65	25-30	730-900		ⓖ ZnS	
② SINTER MACHINE	100% < 10	0.4-4.5	140	320-700	DEW POINT: 122-140		ⓖ ZnS, PbS, CdS

FIGURE 2-10B Zinc Smelting Flow Diagram

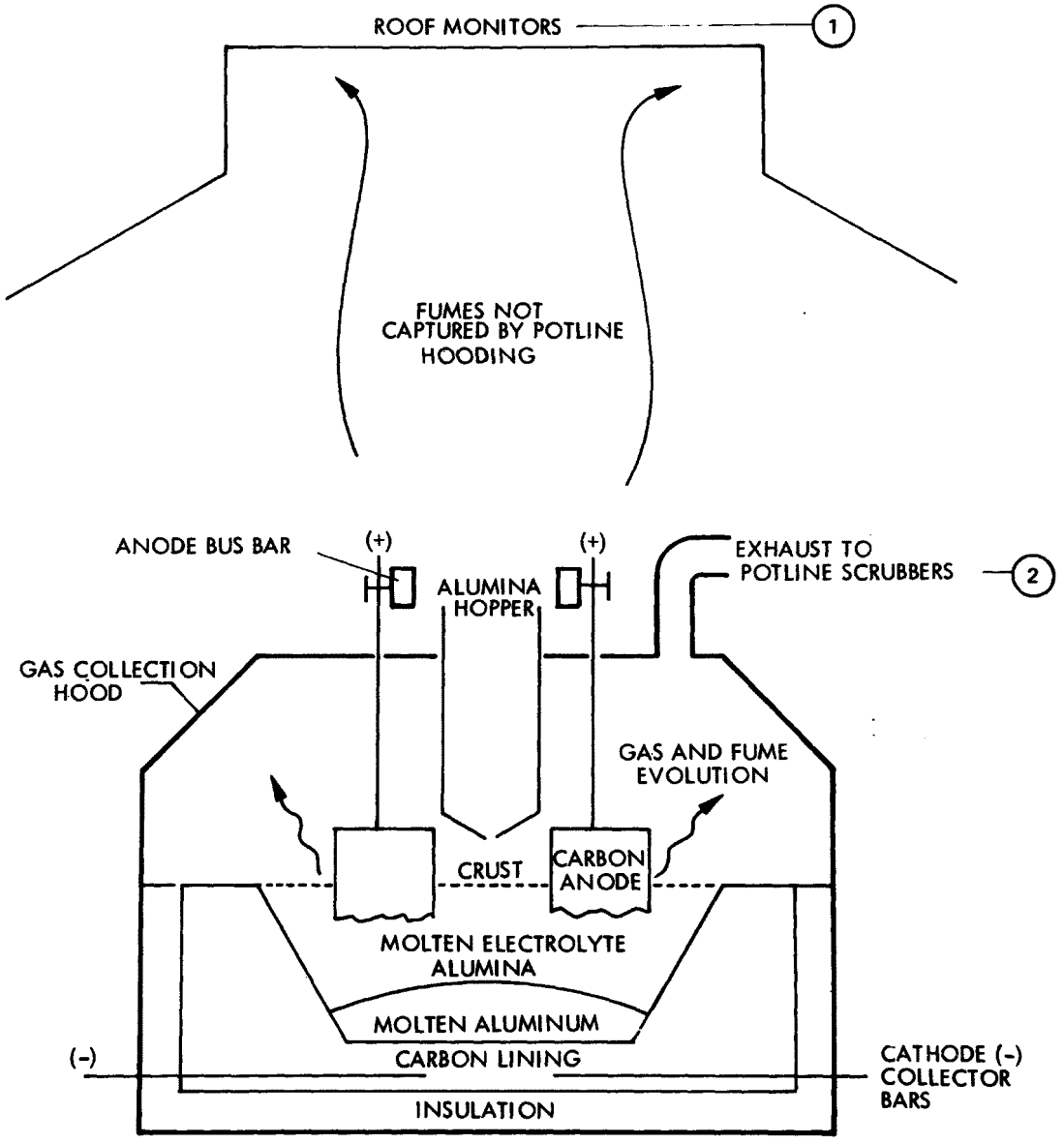


FIGURE 2-11A Aluminum Cell (Prebaked Anode Type)

POTENTIAL PROCESS SAMPLES

① ⓐ GAS: TIME INTEGRATED
ⓑ GAS: FUGITIVE EMISSIONS [SPECIFIC SOURCE]
② ⓐ GAS: PARTICULATE MATTER [ON EXHAUST]
ⓑ LIQUID: INTEGRATED COMPOSITE

	EFFLUENT CHARACTERISTICS FROM PREDOMINANT PROCESS OPERATIONS					REDUCED SPECIES PRESENT IN PRIMARY EFFLUENTS	
	PARTICULATE DATA						
PROCESS IDENTIFICATION	SIZE DISTRIBUTION	gr/SCF	FLOW RATE	TEMPERATURE °F	MOISTURE: VOL %	CITED FROM LITERATURE	PROBABLE STREAM BASED ON CHEMISTRY
ⓓ ALUMINUM	SUBMICRON PARTICULATE		2000 to 4000 CFM/ CELL			Ⓖ	Ⓖ
① REDUCTION CELL		0.03-2.0				H_2S	COS, Na_2S, CaS, Al_2S_3 ELECTRODE IS CONCERNED IN THE REDUCTION PROCESS; CONSIDERABLE CO IS FORMED. METAL CARBONYLS MAY THEREFORE RESULT.

FIGURE 2-11B Aluminum Cell (Prebaked Anode Type)

Table 2-2
Selected References for Process Information

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SECTION 3.0

SAMPLING TECHNIQUES FOR REDUCED INORGANIC SPECIES

The sampling procedures described in this section have been chosen for the processes listed in Section 2.0 with a view toward obtaining samples that will afford an analytical accuracy of ±25%. Simply stated, an accuracy level of ±25% requires adherence to the following three practices:

- Samples must be time integrated to account for process operational variances.
- Sampling techniques must be sensitive enough to measure volumes, weights or flows with greater accuracy than ±25%.
- Careful attention must be given to the avoidance of sample contamination and/or loss.

The sampling techniques recommended in this study have been chosen to characterize specific streams for the processes presented in Section 2.0 and include:

1) Solid: integrated conposite
2) Liquid: integrated composite
3) Gas: time integrated (non-particulate)
4) Gas: fugitive emissions
5) Gas: SASS train (particulate)

At this time certain general comments may be made concerning these five techniques with respect to obtaining samples containing reduced inorganic species. Final decisions concerning exact sampling methods for a site will require a more detailed study of the individual process chemistry and stream parameters. Many of the methods eventually selected will have to be novel techniques tailored to the characteristic unstable

and/or reactive nature of many reduced inorganic species. The sampling techniques selected for use must have the potential to maintain the constituents of a sample in their original state or in a controlled modified state which can then be related in a quantitative manner to the original compound structure.

3.1 SOLID: INTEGRATED COMPOSITE

Solid samples may be obtained by using shovel or core sample techniques over a time period representative of the cyclic nature of the process in question. However, automatic sampling techniques should be used whenever available if they meet the ±25% accuracy criterion. If the process is not cyclic, samples should be taken at equally spaced time intervals for a specified time period. The composite thus obtained should be reduced using a coning and quartering technique to obtain a final sample for shipment to the laboratory.

Coning and quartering consists of carefully piling the material into a conical heap then flattening the cone into a circular cake. The cake is then divided into quadrants with opposite quadrants being taken for the representative sample and the other two discarded. The entire process can be repeated until the desired sample size is obtained. This method is time consuming and the symmetry of the intended vertical size segregation may be difficult to achieve in practice. An alternative method is called fractional shoveling, in which every third, fourth, fifth, or tenth shovelfull is taken as a sample. This method is applicable to materials being loaded, unloaded, or moved from one place to another by shoveling. If performed conscientiously, fractional shoveling can be more reliable than coning and quartering and is inexpensive and relatively fast.

3.2 LIQUID: INTEGRATED COMPOSITE

Accurate and representative liquid samples are best obtained by collecting hourly increments of 0.25 liter. The total quantity of the sample increments collected should be approximately 0.1% (but not more than 105 liters) of the total quantity of the stream being sampled.

If automatic samplers are available for the streams in question, they should be used in accordance with the plant production schedule as a first perference. Many liquid streams contain suspended particulate matter. If an accuracy level of ±25% is to be obtained, these streams must be sampled isokinetically using a time integrated continous sampling technique. There are several designs for continuous sampling probes, a few examples are shown in Figure 3-1 below.

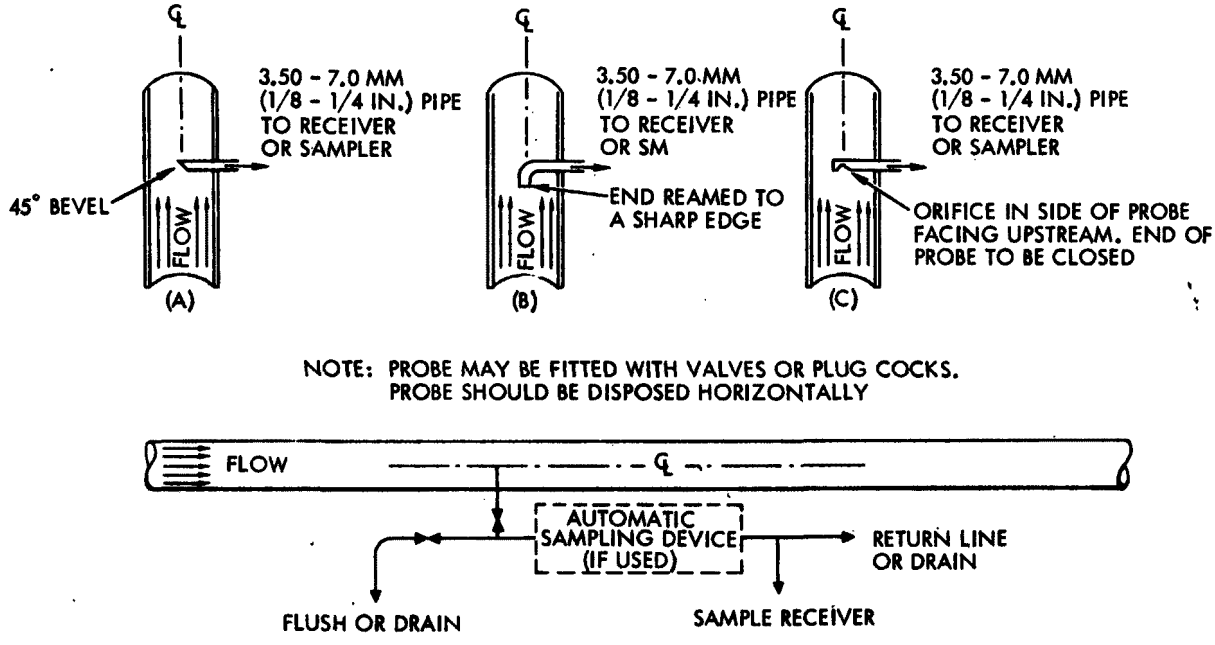


Figure 3-1 Probes for Continuous Liquid Sampling

3.3 GAS: FUGITIVE EMISSIONS

Sampling for fugitive emissions around a plant may involve sampling vents (atmospheric and high pressure), closed areas surrounding a specific pollutant source (the building housing an open hearth), and the boundaries of the plant in a carefully designed matrix. Vent systems generally consist of relief tubes or exit ducts regulated by in-line pressure relief valves. Vents of this type are found in holding tanks and storage tanks and are usually released into the air when the tank pressure exceeds the pressure setting of the in-line valve.

In order to obtain a representative fugitive emission sample from a specific source it is important that:

- The sample be taken while the vent cycle is in progress. (Cycle periods for individual processes should be known as a result of a pre-test survey).
- The entrance nozzel of the sampling unit be situated in such a way that a representative sample of the vent effluent is obtained without contamination by ambient air.

Manufacturing, process, or transfer areas either enclosed or open are major sources of fugitive emissions. Depending on the control devices in use, the emissions can range from slightly above ambient to near stack gas levels. In all cases, the duration of the sampling period should be integrated with the cyclic nature of the processes.

In obtaining fugitive boundary samples, the perspective is considerably altered with respect to the methods which apply to enclosed structure sampling. Depending on the size of the plant in question, there may be a multitude of isolated sources each of which contribute to the overall emission. Atmospheric mixing will play a role in homogenizing individual emission sources, but certainly not to a reliable and predictable degree.

It is generally recommended that at least four sample points be established at equal distances apart in such a way that if the process under investigation were quartered, each quarter would be represented by one sampler. If the plant is larger, it can be divided into sixths with one sampler for each sixth or more depending on the size of the installation to be sampled. Consequently, in order to obtain reliable data the decision as to the position and number of samplers and the sampling time should be based on:

1) The analytical objectives for the acquired samples (if ±25% analyses are to be performed, then sampling accuracy must be of at least this order).

2) The total land area of the process in question (larger plants will require a greater number of sampling points to provide the proper coverage. Too few sampling points in a large plant could miss emission point sources (stacks, vents, etc.) due to

meteorological conditions).

3) The number of emission sources within the system (in order to avoid a biased sample when many emission sources exist within the plant boundaries, the number of sample points should be increased).

4) The estimated average fugitive emission concentration (many situations will require long sampling periods to obtain enough sample for analysis. Thus, the time required to sample will vary inversely with emission concentrations).

5) The number of enclosed structures in which emission levels are expected to be high (when more sources of different emissions exist, the network of samplers may also have to be increased to obtain representative samples).

6) Cyclic nature of emissions (most plants will have operations that vary with time. The sampling team has the choice of sampling for a period of time to overlap the cycles or to time the sampling period to the cycle).

3.4 GAS: TIME INTEGRATED

Many reduced inorganic species of interest may be found in the gas (non-particulate) phase. Special techniques will be required to sample for these compounds. Conventional time integrated bag samples or metal sampling systems probably will not prove to be adequate for traping reduced species because of the unstable or reactive character that these compounds often exhibit.

In view of the accuracy requirements ($\pm$25%) the samples will, however, have to be time integrated. Chemical adsorption impinger sampling, or on-line analysis when available, have the highest potential as sampling techniques for gaseous effluents.

3.5 GAS: SASS TRAIN

The SASS train, as it is currently configured, is probably not a

viable sampling tool for reduced inorganic species because of the materials used in its construction. Sampling for solid inorganic species from particulate material may be possible using the SASS train, however, reduced inorganic gases will probably either be lost or chemically modified due to their thermal instability or susceptability to oxidation.

In view of the wide spread use of the SASS train and the doubts associated with the use of the SASS train to trap reduced inorganic species in a state that is useful for subsequent analysis and identification, the chemistry of some of the compounds of interest was studied in order to prepare a map of the probable location of specific species in the train. The following sections describe the results of the study.

3.5.1 SASS Distribution of The Hydrides; PH_3, AsH_3, and SbH_3

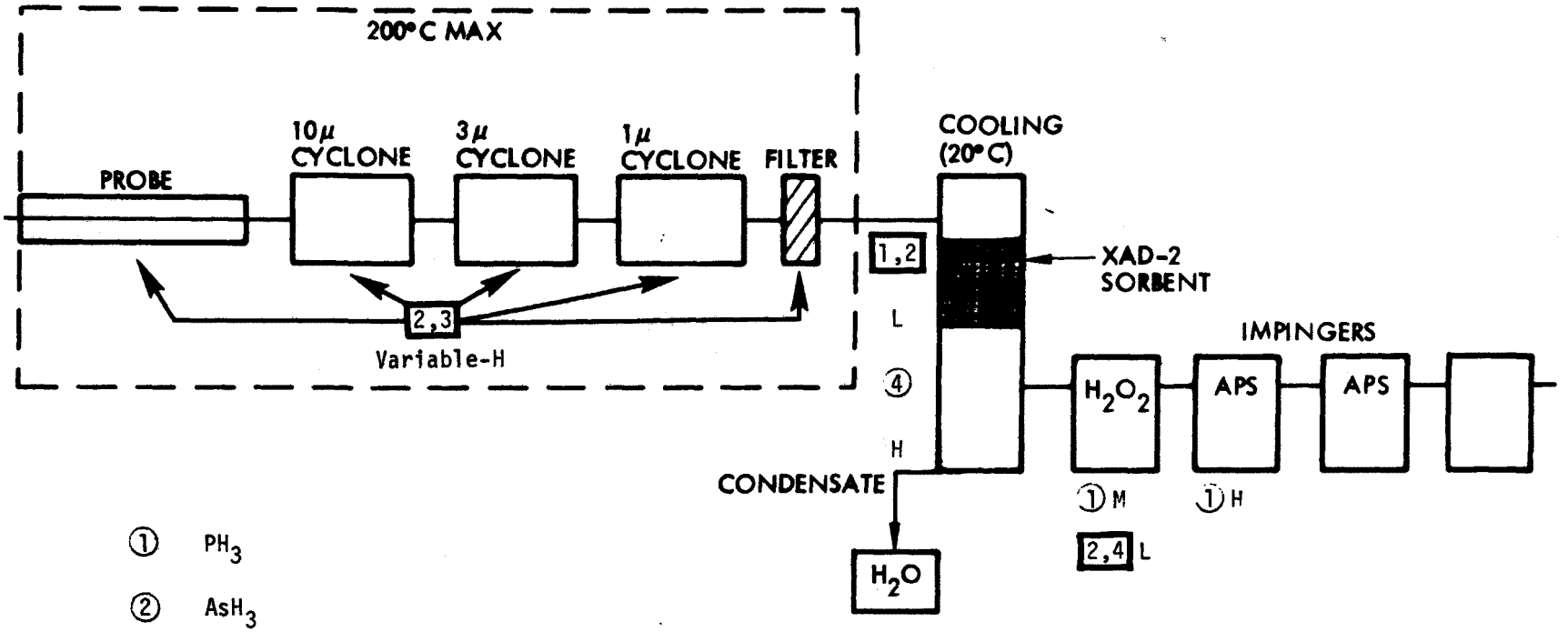
The hydrides (phosphine, arsine, and stibine) can be formed in several processes, for example, in a reducing acidic atmosphere when the respective elements are present or by several electrolytic processes. The stability of these hydrides decreases in the order, $PH_3 > AsH_3 >> SbH_3$, so that stibine is very unstable, thermally decomposing to the metal under mild heat.

In general, the SASS train would be ineffective for sampling these highly reactive substances for subsequent compound identification while sampling techniques which take advantage of the strong reducing character of this series of gases would be perferable. The expected small concentration of these compounds also dictates the use of micro techniques so that subsequent analysis can be performed without excessive preconcentration. A schematic representation of the probable distribution of the hydrides is shown in Figure 3-2.

PH_3 (Phosphine) --

Phosphine, the most stable of the hydrides studied, is not spontaneously flammable but is readily oxidized by air upon ignition. The compound is exceedingly poisonous, sparingly soluble in water, and is a strong reducing agent.

Based on the chemistry and volatility of phosphine, it is not expected



① PH_3

② AsH_3

③ SbH_3

④ Organometallic forms of P, As, and Sb

L = Small concentration

M = Moderate concentration

H = Large concentration

FIGURE 3-2 Probable Distribution of PH_3, AsH_3 and SbH_3 in the SASS Train

to be found at any appreciable concentration in the probe, cyclones or filter. Some PH_3 may react with oxidizing agents, such af Fe (III), to form H_2PO_3 or H_3PO_4 in the presence of water. This reaction is catalyzed by base, but will proceed slowly even in a neutral or acidic medium. The phosphine concentration is also expected to be small in the XAD-2 sorbent trap because of rapid breakthrough. However, no chemical alternation should take place at this point if the atmosphere remains reducing. To analyze phosphine from the sorbent trap, it would be necessary to remove a portion of the resin and chromatograph the contents directly. This can be done in several ways but all involve significant difficulty and result in poor detectability. This analysis would have to be performed on site prior to extraction of the trap for organics. Phosphine will be lost under normal conditions of handling and extraction of the XAD-2 resin.

The solubility of PH_3 in water is very small and none is expected to be found in the condensate. As mentioned above, phosphine is an effective reducing agent and for this reason, it is expected to be found in the first impinger trap. The reaction with H_2O_2 will yield phosphorous and/or phosphoric acid. The reaction would be quantitative if the impinger were basic and for this reason a portion of the PH_3 may survive to be trapped in the second impinger. Analysis of the impingers at this point would only yield total phosphorus of all forms in the effluent stream and could not be directly related to PH_3 in the original gas stream.

Phosphine may be generated by the direct reaction of elemental phosphorus with hydrogen at elevated temperatures (>300°C), increased hydrogen pressure tends to yield much greater quantities of the gas. A small amount of diphosphine is often produced when PH_3 is generated, and is pyrophoric. Phosphine is sparingly soluble in water and shows only a slight tendency to produce the phosphonous ion $(PH_4)^+$. When the phosphonous ion is formed it is very unstable and could not be determined in a "real" sample.

AsH_3 (Arsine) --

Arsine is extremely poisonous and is readily decomposed by heat to arsenic, which is deposited on hot surfaces as a metallic mirror. The decomposition temperature of arsine to arsenic is reported to be 300°C,

however in the presence of metal surfaces or impurities, the reaction can take place at lower temperatures.

If any arsine were to survive passage through the probe, cyclones, and filter its distribution should resemble that of phosphine. Problems of analysis for arsine in the sorbent trap are also similar to those of phosphine which have been previously discussed. Arsine is a more powerful reducing agent than phosphine and would not be expected to exit the first oxidative impinger. Any arsine which reaches the first impinger would be converted to arsenous acid, a stable form of arsenic sutiable for analysis by specialized atomic absorption techniques.

Arsine is not formed by direct reaction of arsenic with elemental hydrogen since the temperatures required for this reaction cause decomposition, however under conditions of very high hydrogen pressure, some arsine may be formed. Arsine is most commonly formed by electrolytic reaction, and may be detected in those industries where such processes occur and arsenic is present. It has also been observed that specific strains of bacteria or fungi can convert organoarsenic compounds to arsine at a level harmful to animal life.

SbH_3 (Stibine) --

The thermal instability of stibine will prevent its passage through the probe. At 200°C stibine is very rapidly decomposed and will be deposited as metallic antimony in the early stages of the train. Analysis for stibine based on its chemistry using the SASS train for collection is virtually impossible.

Due to its thermal instability stibine tends to be formed in those processes where electrolytic or catalytic reactions are performed. Metal refineries where water comes in contact with hot antimony containing materials tend to produce stibine. Stibine is also generated during the charging of batteries contaminated with antimony. Stibine decomposes even at room temperature, so hazards associated with exposure are usually related to close work or confined areas.

Organometallic Forms of P, As, and Sb --

In general, the organometallic forms of the elements are more stable

than the hydrides. The degree of substitution (RMH_2, R_2MN or R_3M where M = P, As, or Sb) increases the boiling point of the compound and also the amount of that compound which may be found in the sorbent trap. An increase in the carbon number of the R group (i.e., $-CH_3$, $-C_2H_5$, $-C_6H_5$) also increases the boiling point of the compound. Analysis for the organometallic forms is possible by GC and/or GC/MS from the XAD-2 resin by direct volatilization, however the concentration of these materials is expected to be very low and micro techniques for trapping may be required for identification and quantitation. Analysis of the bulk of the sorbent trap will generally yield no data on organometallic forms, due to the low level of material expected to be present in most sources.

3.5.2 SASS Distribution of Reduced Sulfur Species

The determination of reduced sulfur species after SASS train sampling should be reasonably effective although quantitative results may be somewhat difficult to obtain because of the distribution of the various forms. After a reduced sulfur species enters the first oxidative impinger, the identity of the parent compound is lost since similar products are formed by oxidation of a number of starting species (see distribution Figure 3-3). Specific cases are discussed below:

H_2S (Hydrogen Sulfide) --

Hydrogen sulfide is a weakly acidic gas and can associate with basic solid surfaces to only a slight degree. It is soluble in water by dissociation and the degree of solubility is pH dependent.

$$H_2S(g) + H_2O \underset{}{\overset{Ka = 9.1\times10^{-8}}{\rightleftharpoons}} HS^- + H_3O^+$$

$$HS^- + H_2O \overset{Ka = 1.2\times10^{-15}}{\rightleftharpoons} S^- + H_3O^+$$

Hydrogen sulfide is a mild reducing agent and in aqueous solution, on exposure to light and atmospheric oxygen, will produce free sulfur by the following reaction:

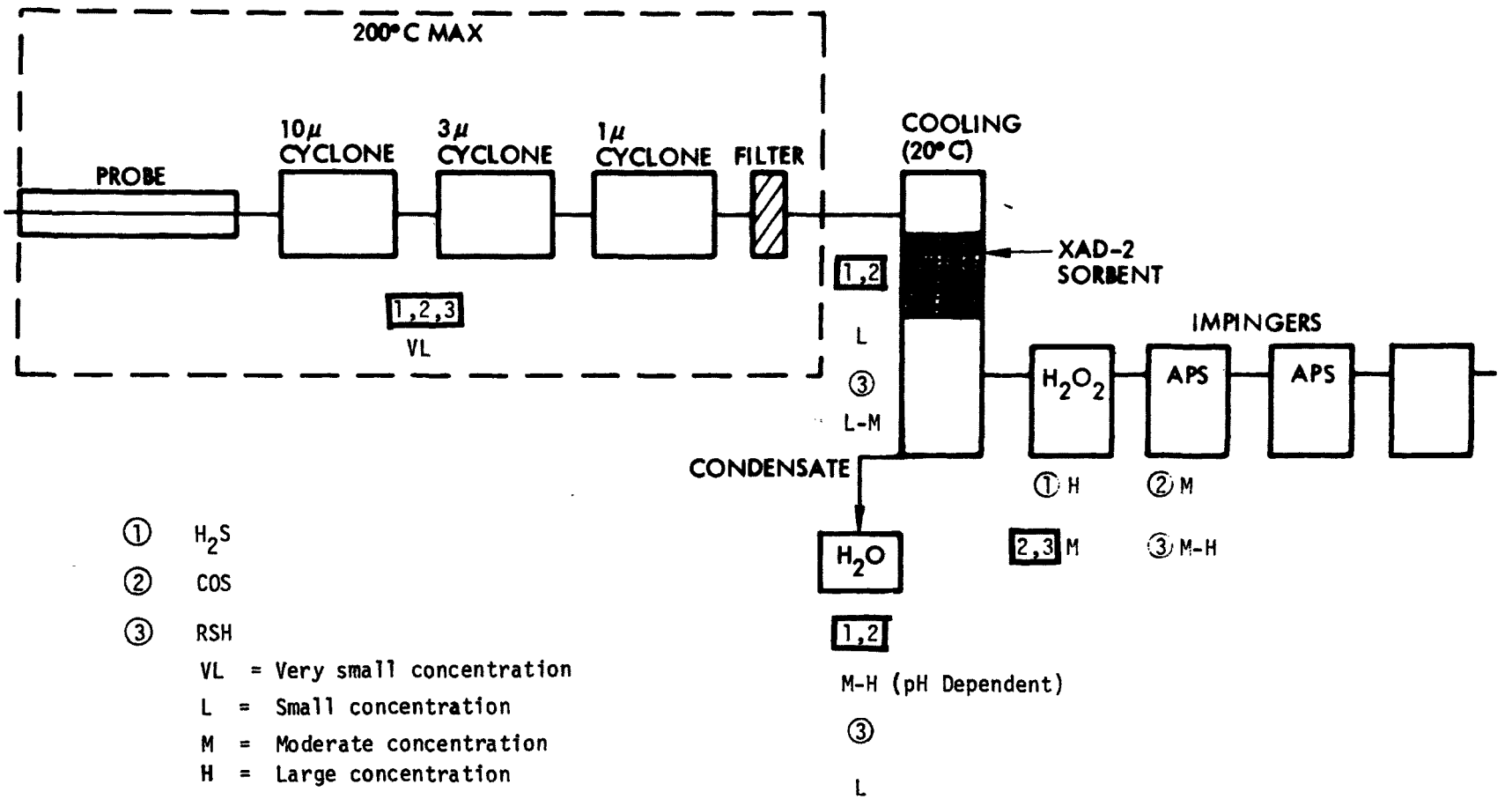


FIGURE 3-3 Probable SASS Distribution of Reduced Sulfur Species

$$2H_2S + O_2 \xrightarrow[H_2O]{h\nu} 2H_2O + 2S$$

Any Hydrogen sulfide in the probe, cyclones, and filter region will be found adsorbed on basic substrates (e.g., flyash). The extent of this adsorption will be limited by the temperature of this zone. Adsorbed hydrogen sulfide can be determined by thermal desorption from the substrate followed by GC analysis. The presence of oxidized species and water can result in oxidation of the H_2S and interfere with the proposed GC analysis by reducing the H_2S levels. The presence of oxidized materials however, is unlikely in a reducing stream where H_2S is expected to be found.

Some hydrogen sulfide may be present in the XAD-2 module. The breakthrough volume for H_2S is rather small and only an equilibrium concentration is likely to be present. Special precautions must be taken to analyze for H_2S present in the XAD-2 module. A portion of the polymer must be thermally desorbed and the H_2S passed to an analyzer (GC or other specific detector). Standard handling techniques and solvent extraction will result in the loss of any adsorbed H_2S in the XAD-2 resin.

A significant concentration of H_2S is expected in the condensate. The solubility of H_2S in water is pH dependent, therefore the more basic the condensate, the greater its capacity for H_2S. The condensate may be analyzed by direct injection gas chromatography using flame photometric detection (GC/FPD) or by acidifying the solution and purging with an inert gas prior to analysis by GC/FPD.

Hydrogen sulfide which survives beyond the XAD-2 trap and condensate module will be entrained in the first impinger. The reaction at this point will produce an oxidized form of sulfur, sulfonic acid, $SO_3^=$, or $SO_4^=$, depending on the nature of other materials present in the impinger. After oxidation the H_2S will be indistinguishable from other forms of sulfur and only total sulfur could be determined.

COS (Carbonyl Sulfide) --

Carbonyl sulfide is a reasonably stable gas which is readily analyzed by several techniques including wet chemical, chromatographic, and

spectrophotometric. Very little COS will be found in the probe, cyclones and filters. Some COS will be present in the XAD-2 trap, however analysis of this sample will be difficult for the same reasons given for H_2S. The major portion of the COS taken from an effluent stream using a SASS train will be present in the condensate due to the solubility of COS in water. This solubility is increased by the presence of organic matter and/or base. A slow decomposition occurs in water, catalyzed by base according to the following reaction:

$$COS \xrightarrow[H_2O]{OH^-} CO_3^{=} + S^{=}$$

Quantative analysis of the COS in the condensate requires rapid analysis after sampling. The decomposition described above will cause errors in both the COS and H_2S analyses.

COS can be analyzed directly by GC/FPD with few interferences, or by spectrophotometric techniques. Carbonyl sulfide can be trapped in a ethanolic solution of piperdine producing piperdine monothiocarbamate which has a distinctive ultraviolet absorption spectrum. This method of sampling will permit the determination of COS, CS_2, and thiophene in the same sample.

COS which enters the impingers will be oxidized, producing CO, CO_2, $SO_3^{=}$, and $SO_4^{=}$. Identification of the original structure will not be possible after oxidation.

RSH (Organo Mercaptans) --

The distribution of mercaptans in the SASS train is dependent on molecular weight, as it relates to volatility. Some relatively small portion of the RSH compounds will be adsorbed on particulate matter. The amount of RSH found in the XAD-2 module will vary according to volatility. Highly volatile materials will pass the module with a minimal volume of gas (low breakthrough volume) while the higher boiling mercaptans will be more effectively entrained. GC/MS is a suitable technique for qualitative identification and quantitative determination of mercaptans from the XAD-2 module. Precautions must be taken in sample handling to minimize loss especially of the more volatile components prior to analysis.

Some RSH compounds are expected to be found in the condensate. Modification of the original compound structure is expected to be minimal, at this point, and similar to that in the module.

RSH compounds which survive to reach the impingers will react in the first impinger and in most cases no correlation with original structure will be possible. Adsorption in a resin filled trap (XAD-2 or Tenax GC) is probably the best method for sampling a complex series of mercaptans. The trap should be followed by a basic impinger to entrain any materials which pass the adsorption trap. An analysis of the material in the trap by GC/MS or GC/FPD will permit direct qualitative and quantitative determination.

3.5.3 SASS Distribution of Reduced Nitrogen Species (NH_3, HCN, and $(CN)_2$)

The reduced nitrogen compounds discussed in this section are generally stable and therefore more readily sampled using the SASS train than some of the other materials previously described. Analysis for specific reduced nitrogen compounds requires special care and techniques for handling the SASS train components to obtain good data on compound type and quantity (see distribution Figure 3-4). The special care required is discussed with respect to each individual compound below. It should be noted that the toxicity of hydrogen cyanide (HCN) and cyanogen $(CN)_2$ is very great.

Ammonia (NH_3) --

Ammonia is a weakly basic gas and therefore its adsorption on acidic substrates is minimal. The presence of water, either vapor or liquid, causes a more basic reaction producing the NH_4^+ ion. Very little ammonia is expected to be found in the probe, cyclones, or filter. Some ammonium salts may be present but no determination of the original form could be made. A small amount of ammonia may be present in the XAD-2 sorbent trap. The breakthrough volume of the gas should be relatively small based on published data of the performance of NH_3 on Chromosorb 101 ®. Contact of NH_3 gas with water will result in effective entrainment and for this reason the highest concentration of ammonia is expected in the condensate. The pH of the condensate will dictate its total capacity for ammonia (the lesser the pH, the greater the capacity) which will be present in the form of the NH_4^+ ion

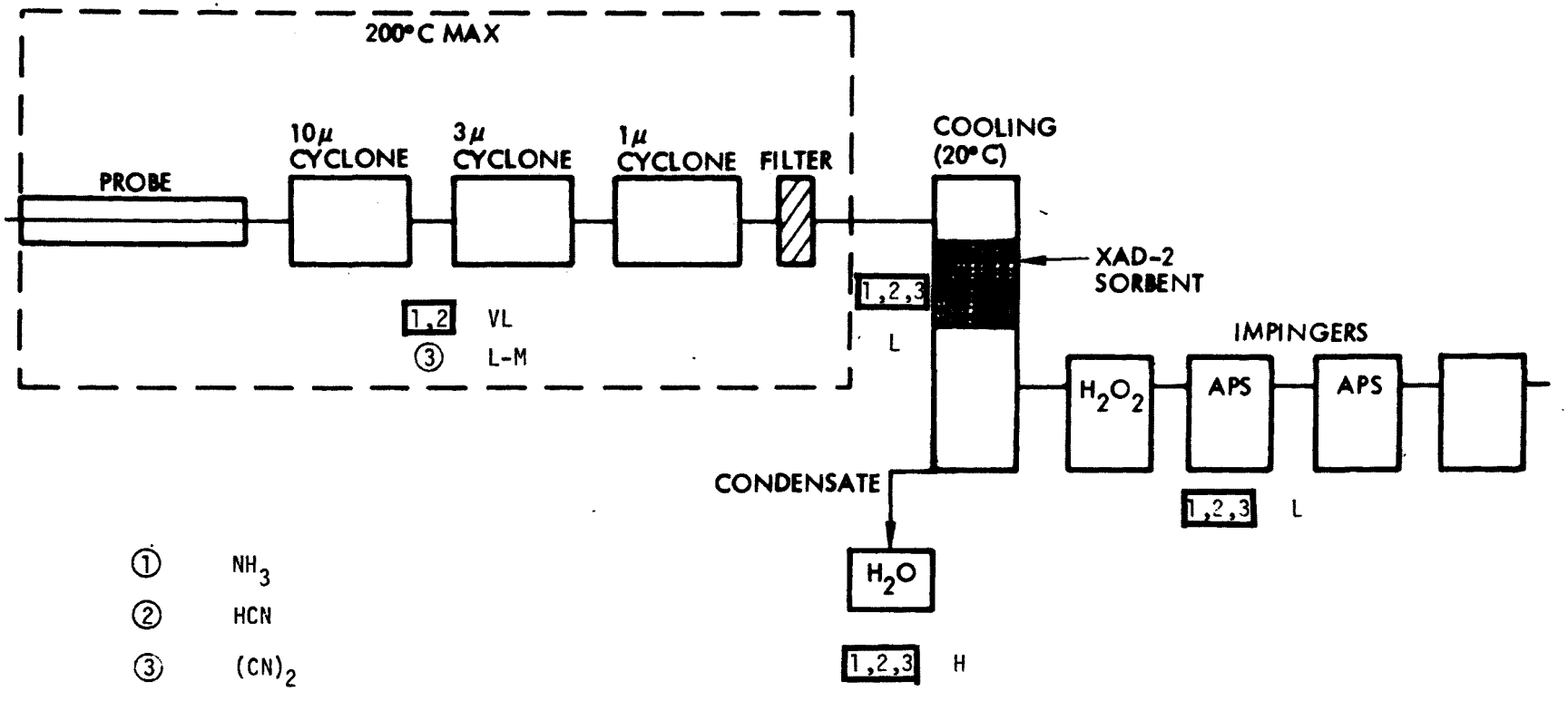


FIGURE 3-4 Probable SASS Distribution for Reduced Nitrogen Species

according to the following equilibrium:

$$NH_3 + H_2O \underset{}{\overset{Ka = 1.8\times10^{-5}}{\rightleftharpoons}} NH_4^+ + OH^-$$

Analysis for NH_3 in the aqueous condensate will depend on concentration. In a very clean system (low contamination of organic matter, etc.) an NH_4^+ specific electrode could be used. For small concentrations, the water sample can be analyzed by direct injection GC. For trace quantities, the sample can be concentrated by raising the pH of the solution and purging to trap the NH_3 on an adsorbent such as Tenax, or Chromosorb 103. Following the concentration step, the sample can be analyzed by GC or GC/MS. Other cleanup and concentration techniques can also be used as dictated by the nature of interfering materials in the condensate.

Analysis for ammonia in the XAD-2 sorbent trap will be more difficult since the NH_3 will be lost if handled using the normal SASS train preparation procedures. If NH_3 in the sorbent trap is to be analyzed, it can be recovered directly by thermal desorption followed by GC analysis, or by extraction with a mildly acidic aqueous solution.

Small quantities of NH_3 may be present in the first impinger. The mechanism for entrainment is based on solubility rather than oxidation. Analysis of this impinger can be accomplished by neutralization and GC separation. After long periods of standing the action of the peroxide on ammonia will decrease the concentration by the production of N_2 and H_2O.

Hydrogen Cyanide (HCN) --

Hydrogen cyanide is a weak acid, highly stable, and very toxic. It is missible with water in which it dissociates according to the equilibrium:

$$H_2O + HCN \underset{}{\overset{Ka = 2.1\times10^{-9}}{\rightleftharpoons}} CN^- + H_3O^+$$

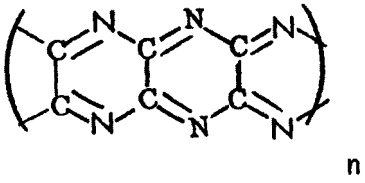
HCN is a liquid at room temperature and has a boiling point of 20°C. In the liquid state it can polymerize violently in the absence of stabilizers. The presence of moisture inhibits this polymerization.

The chemistry of HCN suggests that it will be found mainly in the liquid condensate, dissociated according to its equilibrium, depending on

the quantity of water in the condensate and the pH. Analysis of HCN can be accomplished by GC using several gas-solid adsorbent columns. If the condensate is very clean, the cyanide can be determined by ion specific electrode techniques. A small amount of HCN is expected to be found in the XAD-2 module. Analysis of this portion of the train for HCN requires the same precautions as outlined for ammonia. An XAD-2 trapped sample can be recovered by extraction with mildly basic water. Only a small portion of the HCN is expected to reach the impingers, where it would be lost due to oxidation and conversion to volatile gaseous products.

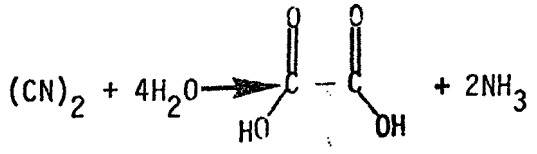
Cyanogen (CN_2) --

Cyanogen is a relatively stable gas at room temperature. Upon heating (300-500°C) it can polymerize to form the ladder structure given below:



The polymer once produced is stable to about 850°C at which point it reverts to $(CN)_2$. Depending on the temperature of the sampled source and the probe temperature gradient, a significant concentration of polymer can be formed and will remain primarily in the probe. Some of this material may also be found in the cyclones and filter, the location being dependent on particle size.

If the polymerization does not occur or occurs only to a small extent, the majority of the $(CN)_2$ is expected to be found in the condensate. Cyanogen is soluble in water but decomposes slowly on standing according to the following, base catalyzed reaction.



The ability to identify and quantitate cyanogen in the condensate depends on the extent of its decomposition reaction which in turn depends

on the time from sampling to analysis. Some cyanogen is expected to be present in the XAD-2 trap and this analysis has the same limitations as those described for NH_3 and HCN above. The toxicity of $(CN)_2$ is very similar to the toxicity of HCN.

3.5.4 SASS Train Distribution for Mercury, Selenium and Metal Carbonyls

Volatile metals pose a special problem for the SASS train which is best suited for organic species and particulate material. Structure identification for volatile metals will be almost impossible due to chemical modification by the train and their expected small concentrations. The toxicity of mercury as the metal is quite great as are most of its compounds. In the case of selenium the metal is reported to possess little toxicity, whereas its compounds are very toxic.

Mercury (Hg) --

The distribution of mercury in the SASS train (Figure 3-5) is dictated mainly by its vapor pressure. Very little of the metal will remain in the probe, cyclones, and filter. Some may exist as amalgams with other metallic forms on the particulate matter collected in the cyclones and filter. The major portion of the mercury will condense at the XAD-2 module and be found in the condensate. Mercury has little affinity for XAD-2, therefore, it would not be found in this portion of the SASS train unless it is trapped in a low spot as a puddle. Mercury found in the condensate should exist as the metal or be converted to the sulfide by the action of H_2S if it is present in the process stream. At this time, it is not clear that an analysis for mercury metal will give accurate results. The possibility of sulfide formation in the train will impose a significant analysis error. The small amount of mercury which is likely to pass the condensate region will be oxidized by the impinger solution and information concerning its original structure on emission will be obscured.

Organomecurials, as governed by volatility, will be found in the condensate region or in the impingers. If present in the condensate, the organomercurials can be analyzed by GC/MS to determine their structure and amount. Organomecurials which reach the impingers will be oxidized and determination of their original structure will not be possible.

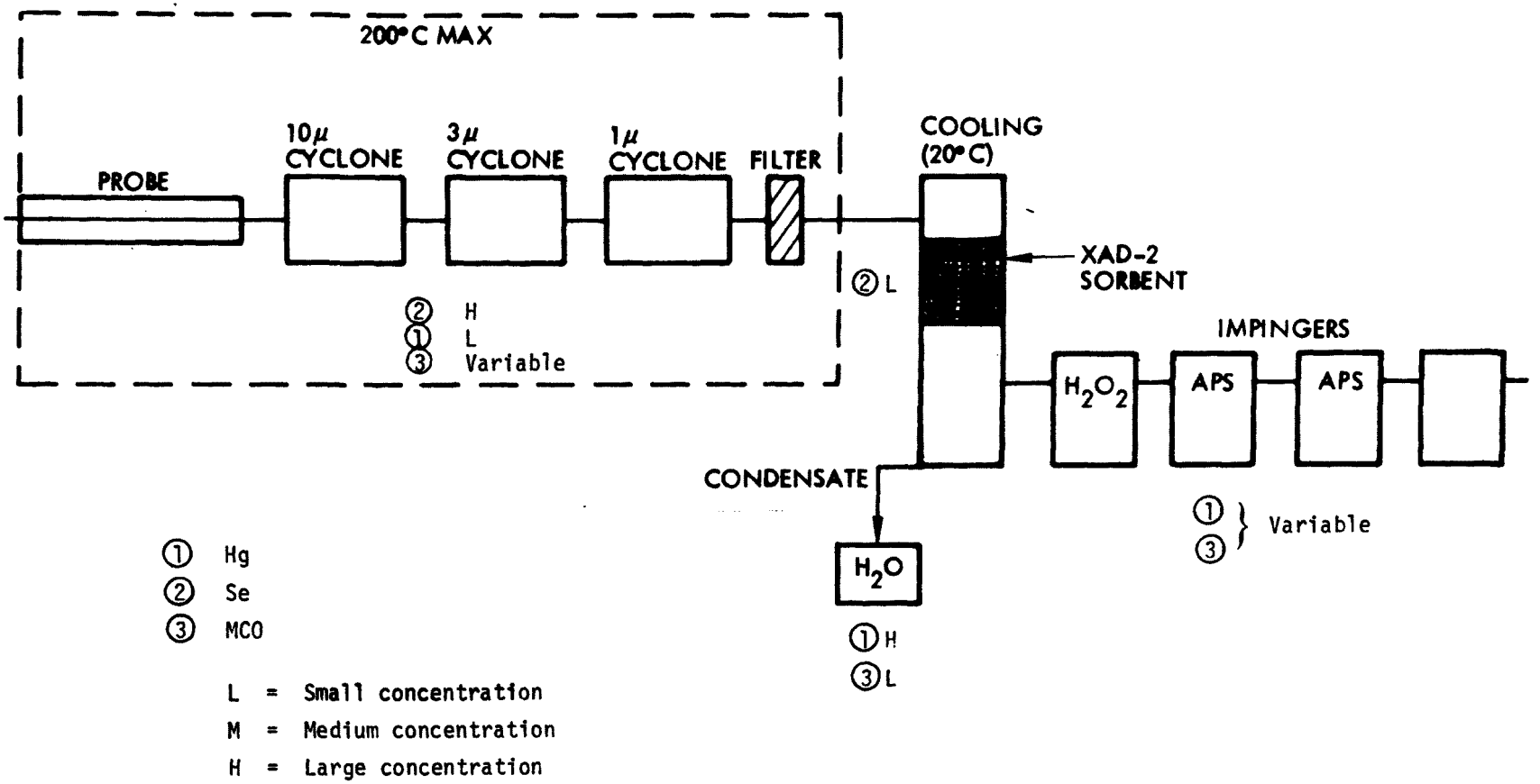


FIGURE 3-5 Probable SASS Distribution for Hg, Se, and Metal Carbonyls

Selenium (Se) --

Selenium is not a particularly volatile metal (melting point =217°C and boiling point =685°C) when compared to mercury (BP = 356°C). It is expected that the majority of the metallic selenium will be in the flyash. Selenium passing through the probe, cyclones, and filter will probably be scrubbed by the XAD-2 module. This action would be the result of simple filtration rather than physical adsorption. Selenium metal is not expected to be found in the condensate or the impingers. Organoselenium compounds and hydrogen selenide, if formed, will be distributed in much the same way as described for mercury. Compound identification would also be virtually impossible if these materials were sampled using the SASS train.

Metal Carbonyls (MCO) --

The SASS train is totally inadequate for the sampling of metal carbonyls. The carbonyls will decompose in the probe, cyclones, or filter according to their stability, yielding the metal and liberating carbon monoxide. The more stable carbonyls may reach the impingers were they too will decompose. Special sampling techniques are required for these materials, followed by compound specific analysis.

SECTION 4.0

SAMPLING AND ANALYSIS OF GASEOUS REDUCED INORGANIC COMPOUNDS

The sampling and analysis procedures presented in this section have been identified from the open literature, developed or modified in the laboratory, and in some cases tested during a field study on an actual source of reduced inorganic emissions. The procedures are detailed and and their application is limited to one or at most a few individual reduced inorganic compounds. Due to the generally unstable nature of reduced inorganic compounds, the procedures require specialized sampling equipment and techniques. For the purpose of sampling and analysis, reduced inorganic compounds can best be divided into groups based on their acidic, basic, or neutral characteristics. Stability of the species to oxidation is also an important parameter as illustrated by the metal hydrides (Section 4.3.1). The species selected for determination in the acidic class include: hydrogen sulfide, mercaptans, and hydrogen cyanide. The basic group consists of ammonia and low molecular amines while the neutral class includes metals, hydrides, cyanogen and carbonyl sulfide.

4.1 SAMPLING AND ANALYSIS OF ACIDIC REDUCED INORGANIC GASES

An understanding of the chemistry of specific compounds to be sampled and analyzed is the first step in establishing methods or recommending procedures. The chemistry of the stream, previously discussed in Section 2.0, from which a sample is taken may also influence methodology to be used.

Hydrogen sulfide is a weakly acidic gas and for this reason associates will base substrates only to a slight degree. The presence of water, however, causes a dissociation of the hydrogen sulfide molecule resulting in water solubility, the degree to which is pH dependent. Hydrogen sulfide is a mild reducing agent which on exposure to light and air in an aqueous

solution will produce free sulfur. Sulfides of many metals are also formed in aqueous solution most of which are insoluble. Care must be taken in the design of sampling equipment to avoid hydrogen sulfide losses due to non-recovered moisture fallout and metal sulfide formation.

Mercaptans behave similarly to hydrogen sulfide, however as the molecular weight of the compound increases its organic character predominates. Low molecular mercaptans are considered in this report as reduced inorganic species but the techniques discussed will decrease in effectiveness as the R group carbon numbers (RSH, R = CH_3, C_2H_5, C_3H_7, etc) are increased. Each individual mercaptan must be considered separately as to sampling efficiency and analysis accuracy. In addition, mercaptans react with metal surfaces and are converted to the disulfide in the presence of air, under rather mild conditions. For this reason extreme care in the design of sampling equipment must be taken.

Hydrogen cyanide is quite similar to hydrogen sulfide in its gaseous and solution characteristics. Like hydrogen sulfide, the solubility of HCN in water is pH dependent. Additionally, HCN is thermally stable and highly toxic both as the gas and in solution.

4.1.1 Sampling Techniques for Acidic Reduced Inorganic Gases

For the purpose of this discussion, sampling will be treated in terms of sample collection, concentration, preservation and introduction to the analysis technique as an off-line batch process. The use of grab techniques for high concentration species and/or on-site analysis will not be addressed in detail. The techniques discussed were chosen to minimize sample contamination, to facilitate sub-ppb determination, to provide for a degree of preconcentration, and to allow for simplicity of application. For the analytical results to be meaningful, sample integrity must be maintained. To achieve this the sampling method must avoid fractionation, evaporation, chemical reaction or biological degradation. It is obvious that the sampling technique will have a great impact on the accuracy, reproducability, limits of detection, and the credibility of analytical results.

Impinger Trapping Techniques for Acidic Reduced Inorganic Gases --

Several impinger solutions were investigated during the course of this

study to determine their ability to entrain acidic gases (i.e., H_2S, HCN, and RSH). The results of these tests show the best impinger solution to be basic cadmium sulfate. Original work on the use of basic cadmium sulfate for trapping hydrogen sulfide was reported by O'Keefe and co-workers [1].

Prior to the evaluation of sampling techniques, standards were obtained (Scott Environmental - H_2S and C_2H_5SH and Matheson - HCN) of the acidic gases to be analyzed. The hydrogen cyanide was obtained in a pure form while the hydrogen sulfide and ethylmercaptan were obtained as dilute mixtures, 100 ppm and 110 ppm respectively, in helium. These standards were used to evaluate the trapping efficiency of the impinger sampling system and to provide samples for the development of analysis techniques.

The apparatus shown in Figure 4-1 was used to introduce pure reduced inorganic gases into an impinger train and to also introduce dilute gaseous mixtures. Two impingers were used in series to obtain samples for subsequent analysis.

During the evaluation phase, samples of a known volume of hydrogen cyanide were slowly added to the impinger train by introduction at the Teflon® tee (Figure 4-1). The results of the impinger train study are present in Table 4-1. The general lack of detected species in the second impinger indicates good trapping effeciency however, if higher flow rates are used the effeciency will probably decrease. Under these circumstances 3 or 4 impingers should be used in series to ensure efficient sample recovery. The effect of interferences on trapping efficiency was not evaluated, however no problems are expected unless the cadmium sulfate is totally consumed during the sampling operation or the basic character of the solution upset. An alternative method for hydrogen cyanide sampling involves the use of concentrated sulfuric acid impingers. The technique has been used successfully to determine HCN in shale oil conversion process effluents (2). The method involves the use of dilute hydrochloric acid impingers to remove ammonia followed by concentrated sulfuric impingers. The concentrated sulfuric acid hydrolyzes the HCN to ammonia. The impinger solution is then analyzed for ammonia by any of several analysis techniques, some of which are discussed in Section 4.2.

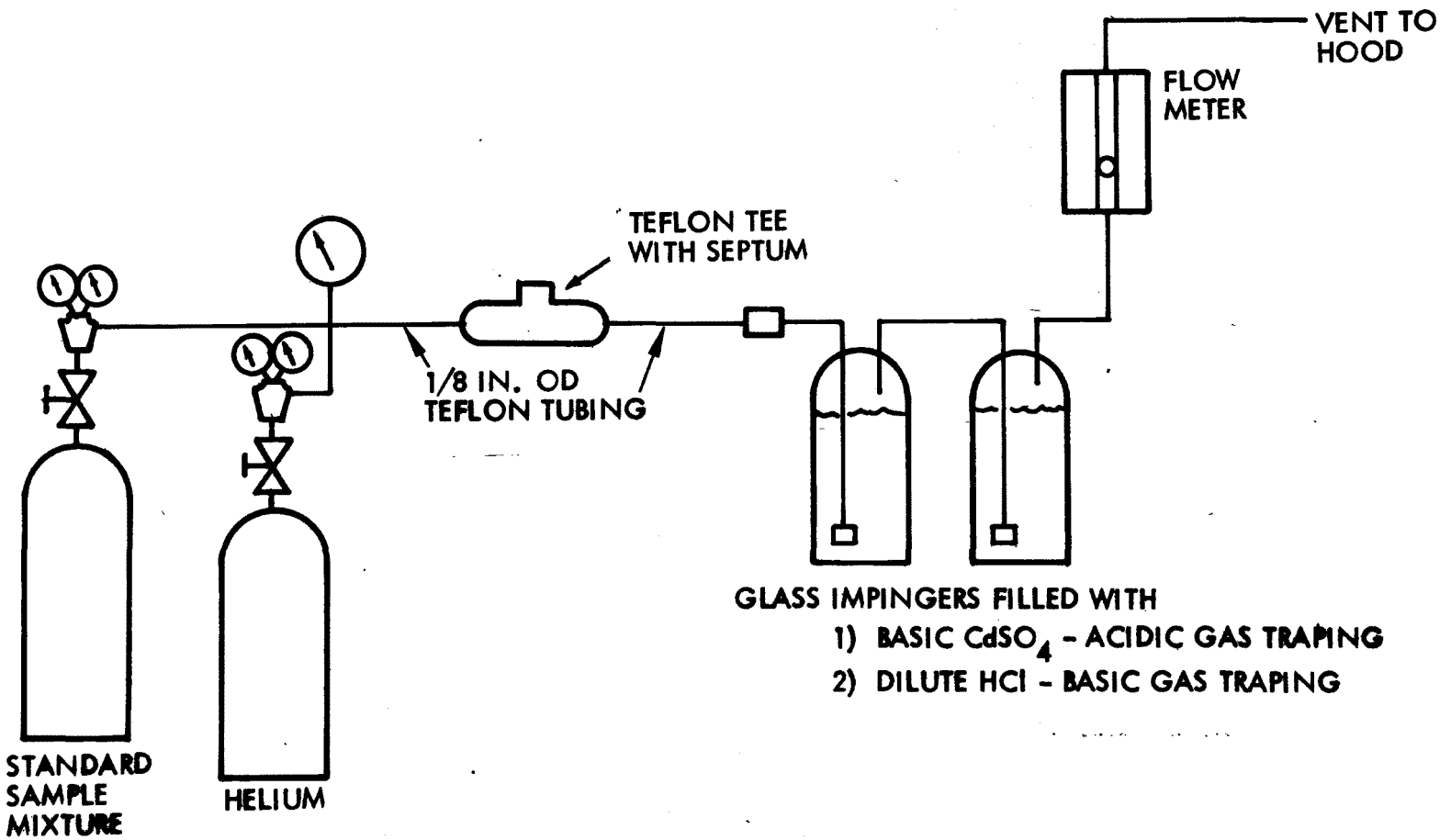


FIGURE 4-1 Sample Preparation Apparatus for Evaluation of Impinger Solutions

Table 4-1

Impinger Trapping Efficiency

Sample	Amount added	1st. impinger	2nd. impinger
H_2S	1 µg	T	ND
	10 µg	yes	ND
	100 µg	yes	ND
HCN	1 µg	T	ND
	10 µg	yes	ND
	100 µg	yes	T
C_2H_5SH	1 µg	T	ND
	10 µg	yes	ND
	100 µg	yes	T

Solid Adsorbent Materials for Sampling Acidic Reduced Inorganic Gases --

The use of adsorbent materials for sampling acidic reduced inorganic gases was evaluated using hydrogen sulfide since it is typically the first compound to elute from most chromatographic columns (i.e., lowest break through volume). Initial studies were conducted using tenax GC and XAD-2. Both of these materials were found to be inadequate for the sampling of H_2S because of very low break through volumes even at reduced temperature ($0^{\circ}C$). One candidate material, Porapak QS, was found to be marginally acceptable at $0^{\circ}C$. A complete evaluation of adsorbent sampling techniques for H_2S was not conducted since liquid filled impingers were found superior for all of the compounds of interest. In addition the impingers provided a more stable and transportable sample for off site analysis.

Grab Sampling for Acidic Reduced Inorganic Gases --

When field analytical equipment is available and the reduced inorganic sample concentration in the effluent stream is relatively high, grab sampling is the prefered method. The rapid analysis in the field results in less expense and the samples do not require significant stabilization.

When samples are taken for laboratory analysis, grab sampling techniques are not recommended. Sample losses due to condensation, leakage, and chemical modification of reactive compounds result in unreliable analytical data. In most cases water vapor is condensed when a grab sample is taken and the presence of water will significantly reduce the concentration of acidic reduced inorganic gases in the vapor phase due to their inherent water solubility. To reduce the effect of water vapor, an ice trap system (see Figure 4-2) is often used. This sampling device will consistantly produce low results unless the condensate in the trap is analyzed together with the gas bags.

4.1.2 Analysis Methods for Acidic Reduced Inorganic Gases

The chemical state of the sampled species often dictates the analysis technique to be used. Impinger solutions, if relatively clean, can be analyzed using ion specific electrodes or classical wet chemistry techniques. For more complex mixtures, regeneration of the original sample gas is often

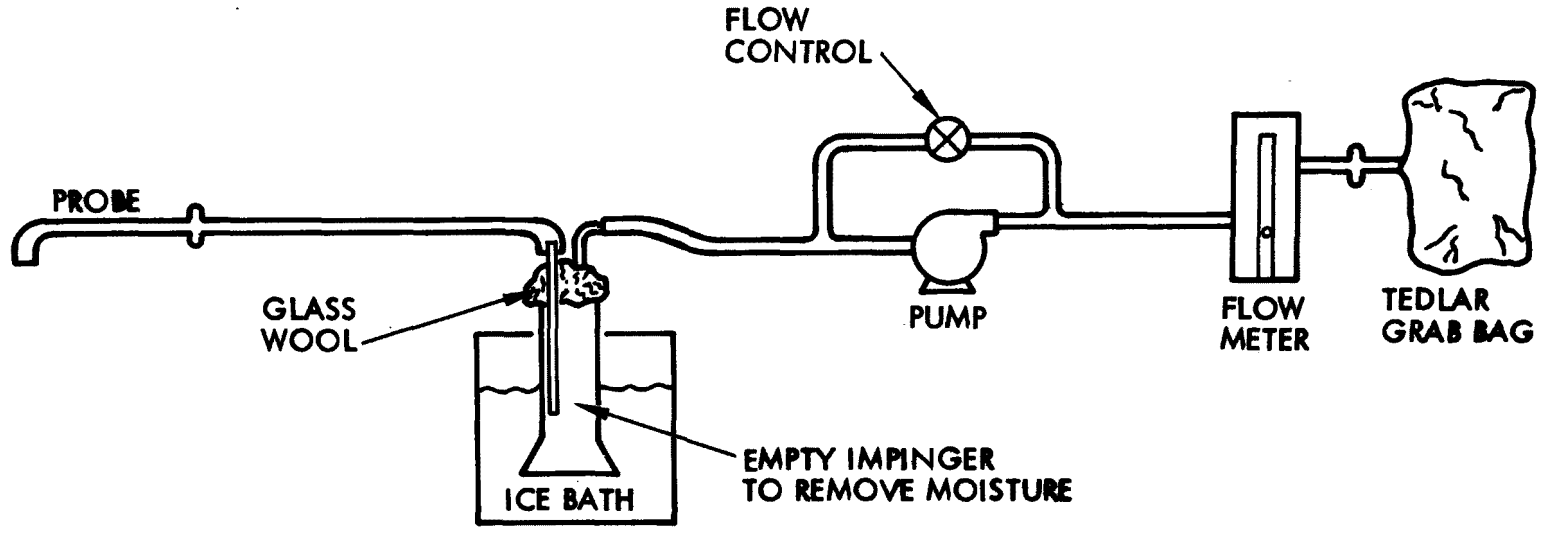


FIGURE 4-2 Typical Grab Gas Sampling System

required to minimize interference problems. For samples adsorbed on solid substrates (adsorbent sampling), thermal desorbtion or extraction with an appropriate solvent may be used prior to analysis. Grab samples may be analyzed directly or after concentration using a solid adsorbent or cryogenic trapping.

The procedure to be used for analysis will be dependent on the matrix from which the sample was taken, possible interferences, and the sampling technique. The following discussion presents techniques currently in use as well as procedures developed as a part of this task.

Analysis of Impinger Solutions for Acidic Reduced Inorganic Gases --

In most cases where "real" effluent streams are sampled, direct analysis of the impinger solutions is impossible due to the large number of interferences. For this reason, it was determined that the best analytical approach was to develop methods in which the sample is returned to its original state. In the case of acidic gases entrained in impinger solution the samples would be regenerated and analyzed as a gas. In this work the apparatus shown in Figure 4-3 was used for the regeneration of acid gases prior to analysis. The procedure for regeneration involves removing a representative aliquot of the impinger solution (the impinger may contain solids which must also be proportionally taken) and placing it in the regeneration flask. A helium purge is begun (100-300 cc/min) and the collection trap cooled. Acid (1M H_2SO_4) is added to the flask to regenerate the gaseous acidic species and to reduce their water solubility. The helium purge is continued for five minutes with mild heating to effectively remove the sample gas.

Several techniques were studied for recovering the sample gas purged from the impinger solutions, including trapping with dry ice/acetone, liquid nitrogen and solid adsorbents. The most efficient combination for sample recovery proved to be a trap packed with Porapak QS and cooled using a dry ice/acetone bath. The total purge gas volume should be kept to a minimum to avoid sample break through and ice formation in the trap. When liquid nitrogen was used to trap the sample gas, the Teflon® valves leaked during the warming cycle apparently due to a significant increase in pressure. Drying of the purged gases using magnesium perchlorate or 5A molecular

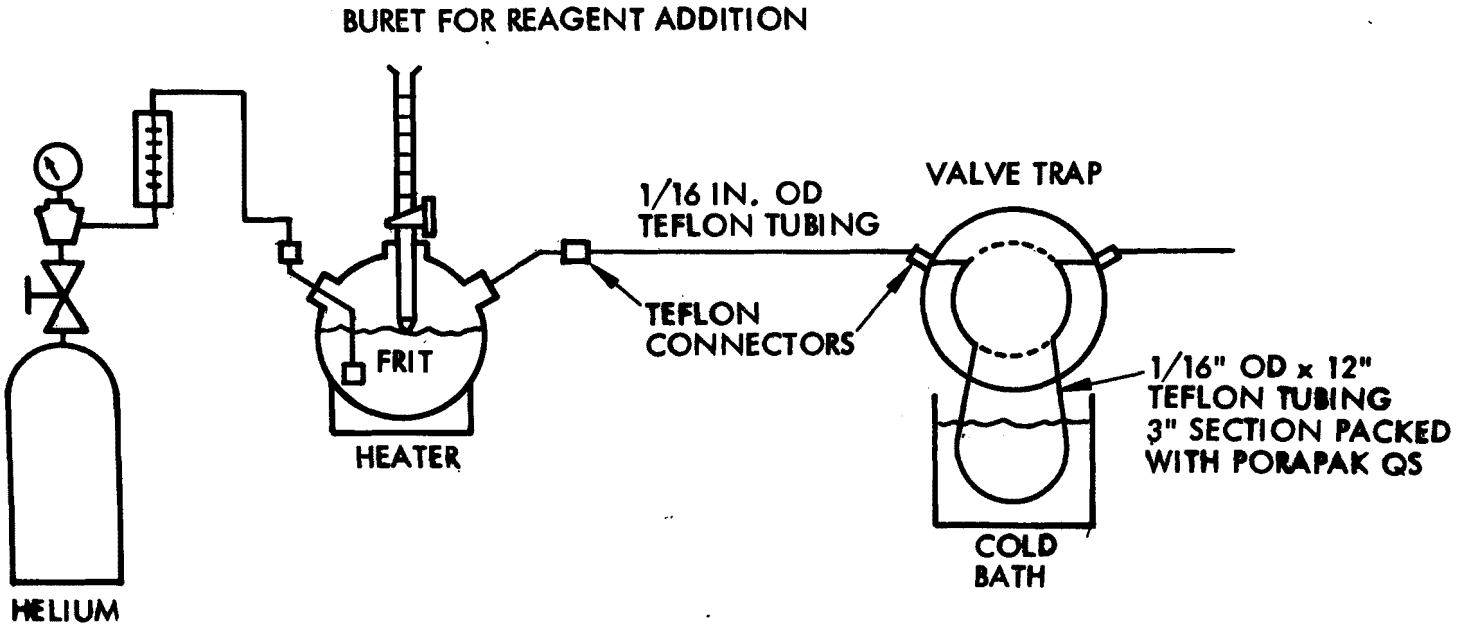


FIGURE 4-3 Regeneration Apparatus for Samples Obtained Using Impinger Sampling Techniques

sieves tended to improve detectability, but further work must be done to determine their effect on compound integrity and quantitative recovery from a variety of samples.

Gaseous separation can be accomplished by either gas-solid or gas-liquid chromatography. The most common packings for gas-solid chromatography include silica gel, alumina, activated charcoal, molecular sieves, and porous polymers. The molecular sieve and porous polymer substrates are most often used. Care must be taken to avoid irreversable adsorption on the solid phase packing which can result in reduced column performance and low calculated recovery. As an example the adsorption of water on a molecular sieve column significantly reduces its separation effeciency and the water can only be removed by baking the column at elevated temperatures with a gas purge.

Gas-liquid chromatography separation requires the gases under study to have different solubilities in the liquid phase. If an approprate column can be found for a specific analysis the resultant peaks tend to be very symetrical as opposed to the tailing peaks common to gas-solid adsorbants. The disadvantage of liquid stationary phases include decomposition by reactive gases resulting in sample loss and excessive column bleed at the higher temperature typically required for analysis. In most cases a general purpose liquid phase is unavailable for separation of reduced inorganic gases.

Analyses of the acidic gases presented in this report were performed using gas-solid chromatography with the conditions for analysis given below:

Column Type: Glass 3M X 4mm i.d.

Column Packing: Porapak QS;80-100 mesh

Injector: 4 Port Teflon ^{R} Valve System

Detector: Thermal Conductivity

Column Temperature: 25°C-120°C@ 8°C/min, after a 10 minute hold at 25°C

After purging the sample from the impinger solution, the trap containing the sample, (Figure 4-3) was heated to 100°C and injected onto the GC column. A typical chromatogram for acidic as well as some neutral compounds is

shown in Figure 4-4. Quantitation was achieved by calibration with standard gases. Recovery for the various acidic gases studied using this impinger technique is presented in Table 4-2. These results include sampling as well as analysis recoveries. The higher recovery for ethyl mercaptan is probably due to its lower affinity for water than the other two species. The losses of HCN and H_2S are probably the result of water condensation prior to the collection trap followed by dissolution of HCN and H_2S in the droplets.

Other techniques for the determination of HCN in aqueous solution include the picrate colorimetric method (3), polarography (4,5), and potentiometry with ion selective electrodes (6). Other methods for the determination of H_2S and mercaptans include titration of the sulfide and/or mercaptide ion with Cd^{++}, Pb^{++}, or Hg^{+} solution (7,8). When this titration procedure is used the sample must have been collected using a KOH impinger rather than the basic $CdSO_4$ impinger discussed previously. In relatively clean solutions both H_2S and mercaptans can be determined by polarography (9), cathodic stripping voltammetry (10), and amperometric titration techniques in the ppb concentration range.

Analysis of Adsorbent Sampled Acidic Inorganic Gases --

Once a sample has been adsorbed on a specific substrate the analysis can proceed in any of several ways. It was determined as a part of this task that the best procedure is to thermally desorb the sample and retrap the acidic gases on Porapak QS using the procedure described for the analysis of impinger samples. The apparatus employed for this procedure is shown in Figure 4-5.

The adsorbent trap used for sampling is heated and purged with helium to remove the adsorbed species of interest. A minimum of both purge time and gas is used to effect the sample removal. The sample is then retrapped in a smaller volume of adsorbent at $0^{\circ}C$. The second trap is then heated and injected onto a gas chromatographic column using the same procedure and conditions discussed for the liquid impinger samples.

Alternatively the contents of the adsorbent trap can be directly injected onto a chromatographic column. In this case peak broadening was found to be excessive and as a result quantitation suffered. Another

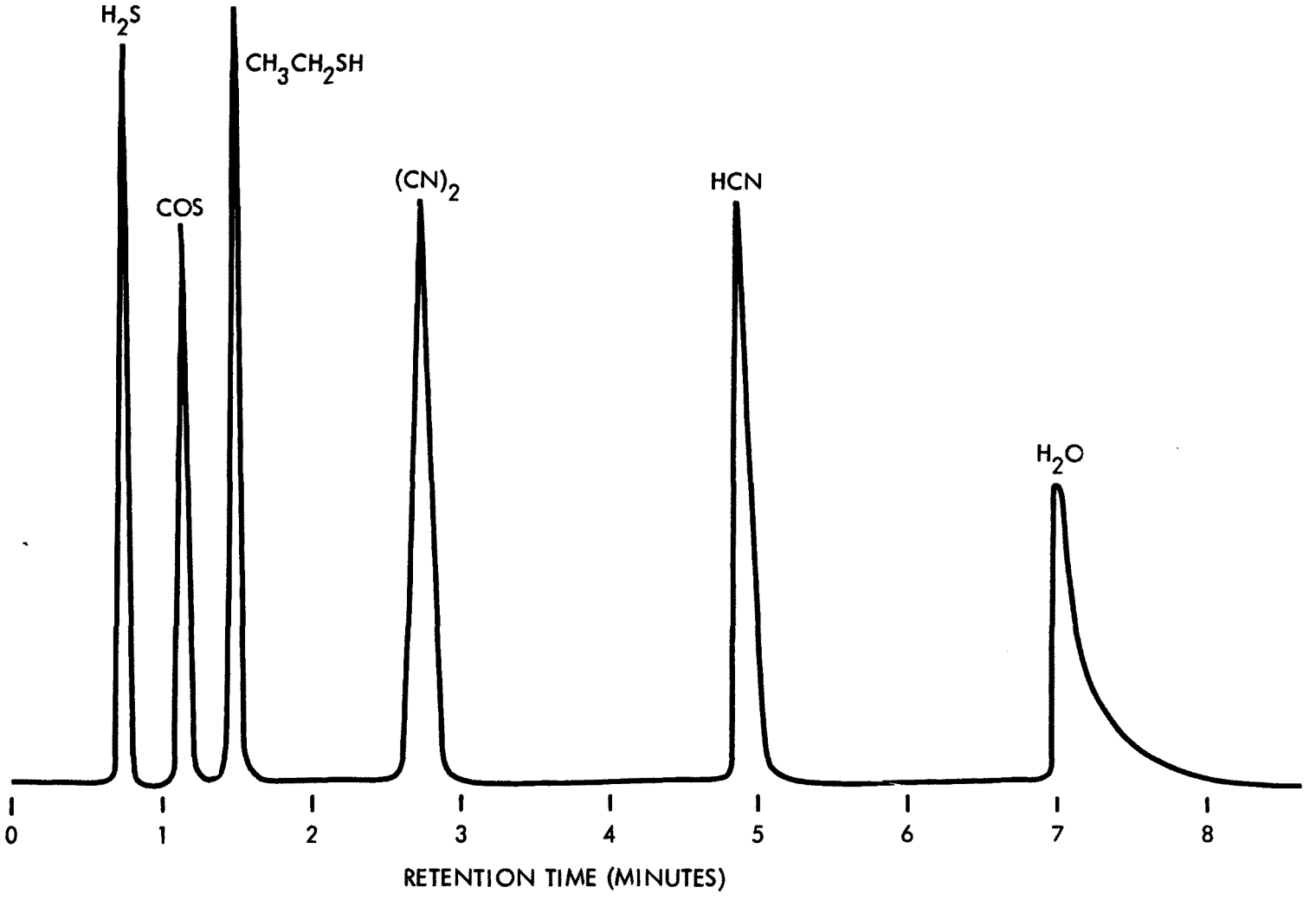


FIGURE 4-4 Typical Chromatogram for Reduced Inorganic Gases Using Porapak QS

Table 4-2

Recovery of Acid Gases From Impinger Solution

Sample	Technique	Recovery
HCN	Acidify and purge	68 - 72%
H_2S	Acidify and purge	71 - 79%
C_2H_5SH	Acidify and purge	81 - 86%

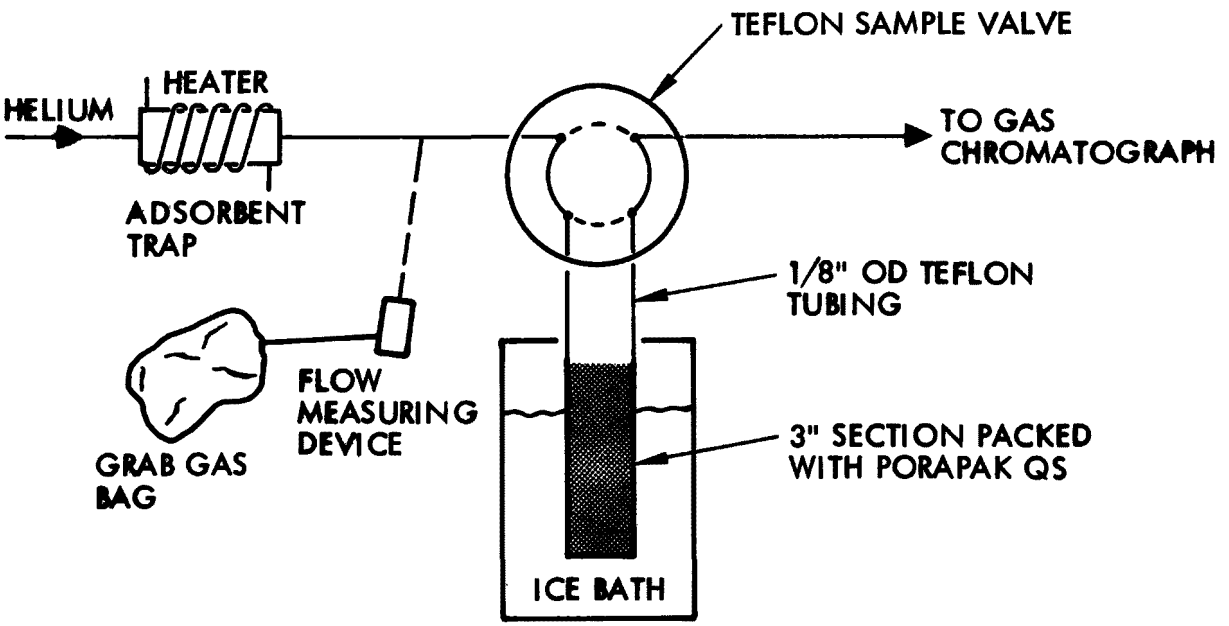


FIGURE 4-5 Resin Adsorption Trap for Preconcentration of Solid Adsorbed or Grab Samples

technique studied involved removal of the sample from the resin by extraction with a basic aqueous solution. Analysis of the resulting aqueous solution can be accomplished in the same manner as previously discussed for the impinger solutions. Low recoveries were experienced in all cases when this procedure was attempted. The low recoveries were probably due to excessive sample handling and inefficient removal of the acidic species from the adsorbent.

Analysis of Grab Samples for Acidic Inorganic Gases --

Grab gas samples can be effectively analyzed on site using gas chromatography techniques. The samples should be removed from the sampling container by expulsion or purging and trapped on an adsorbent as previously described (Figure 4-5). This technique allows for a rapid injection of the sample into the gas chromatograph. The conditions to be used for the gas chromatography are the same as those discussed above.

Interferences are a significant problem when grab samples are analyzed. To minimize the effect of these interferences, selective GC detectors are recommended. The flame photometric detector is quite sensitive to the sulfur species being studied as well as COS and CS_2. The nitrogen/phosphorous (N/P) alkali flame detector is very sensitive to HCN. Cyanogen also responds on this detector but NH_3 does not. The use of selective detectors may be required if the organic content of the grab sample is high and the impurity peaks elute in the same retention window as the reduced species of interest. Significantly more expense and skill is involved with the application selective detectors, especially in the field. For these reasons their use should be limited. In most cases off-site analysis of complex samples is recommended over sophistocated on-site analysis for cost effectiveness.

Table 4-3

Summary of Gas Chromatography Procedures for HCN

Reference	Column	Column Oven Temperature (°C)	Carrier Gas (ml/min)	Detector	Remarks
11	3/16" X 6' Porapak Q	50	N_2(75)	FID	-
12	1/4" X 8' - 25% Triacetin on Chromosorb P	75	He(108)	TCD	-
13	1/4" X 12' - Porapak R	109	He(1)	TCD	-
14	5/16" X 7' - 20% Polyethylene Glycol (PEG) 1500 on Chromosorb	104	H_2(160)	TCD	Column degraded by water

(1) Flow rate not specified.

4.2 SAMPLING AND ANALYSIS OF BASIC REDUCED INORGANIC GASES

Ammonia and low molecular weight amines are the only basic gaseous species considered as a part of this study. Ammonia is a weakly basic gas and as such adsorbs on acidic substrates only to a small extent. The presence of water however, either vapor or liquid, produces a more basic reaction producing the NH_4^+ ion by the following equilibrium.

$$NH_3 + H_2O \underset{}{\overset{Ka = 1.8 \times 10^{-5}}{\rightleftharpoons}} NH_4^+ + OH^-$$

Because of its high solubility in water ammonia is most often sampled by entrainment in an acidic (HCl) impinger and analyzed by titration or by gas chromatography. Thermal conductivity detection is typically used when amines and ammonia are analyzed by gas chromatography. Other specific detectors such as thermionic (N/P) cannot be applied since they do not respond to ammonia.

4.2.1 Sampling For Basic Reduced Inorganic Gases

The three sampling methods previously discussed; impingers, adsorbents and grab sampling, are also commonly used for ammonia and low molecular weight amines. The best technique studied is the entrainment of ammonia in a impinger containing dilute HCl. The direct adsorption techniques suffer from interferences and breakthrough at rather low sample volumes. Grab samples suffer great losses of NH_3 due to high water solubility. Condensation of water in the grab sample container is common and for complete analysis any condensate as well as the gas must be analyzed.

Impinger Sampling for Gaseous Amines --

A large number of impinger solutions for the entrainment of basic reduced inorganic gases were investigated during the course of this study. The most effective impinger solution proved to be a dilute solution of acid in water. Ammonia and most low molecular weight amines have significant water solubility and in an acidic solution protonate to form the ammonium ion increasing solubility. Figure 4-1 shows the test apparatus used for

evaluation of impinger trapping efficiency for ammonia and the low molecular weight amines. Both ammonia and dimethylamine were used in the evaluation. The results prove that, to the detection limit of the analysis technique, both compounds are 100% retained in the first impinger solution. Problems with the subsequent analysis of ammonia and dimethylamine after impinger sampling are discussed in Section 4.2.2. A field test of the impinger sampling technique was conducted at the Paraho Oil Shale Demonstration Plant.

Solid Adsorbent Materials for Sampling Basic Reduced Inorganic Gases --

The use of solid adsorbent materials for the sampling of basic reduced inorganic gases was evaluated using ammonia as the model compound since it typically has the lowest retention volume of the basic species to be analyzed. As a result of these tests, Chromosorb 103 was identified as a tentative candidate for the trapping of low molecular weight amines. Although Chromosorb 103 was found to be best, the breakthrough volume is rather low and temperatures of $0^{\circ}C$ are required to achieve reasonable sample size. If the concentration of ammonia in the effluent gas stream is high, the solid adsorbent technique provides a convenient means of sampling, however when the ammonia concentration is low adsorbent sampling is totally inadequate. For these reasons further tests using adsorbents was suspended since impinger sampling proved to be much superior over a broad range of sources and effluent concentrations.

Grab Sampling for Basic Reduced Inorganic Gases --

Grab sampling is the obvious preferred method when the analysis of samples in the field is required. This technique is effective in sampling most inorganic gases when the concentration in the effluent stream is relatively high. The difficulty with sampling for ammonia by this technique stems from its high solubility in water, which typically condenses in the grab sampling container. Sample losses due to this effect can be extremely high if the water vapor is not removed from the grab container by washing prior to analysis.

4.2.2 Analysis of Impinger Solutions for Basic Reduced Inorganic Gases

Attempts to remove ammonia from acidic aqueous impinger solutions by first making the solutions basic then purging with an inert gas proved to be inadequate. The recovery apparatus previously discussed and shown in Figure 4-3 (Section 4.1.2) was initially tested for the removal of ammonia from impinger solutions. The procedure used involved making the impinger solution basic (1 M HaOH) and purging with helium while the solution was being heated to about 100°C. The evolved ammonia was to be trapped in a Chromosorb 103 filled tube cooled in an ice bath (0°C). When the trap was allowed to warm to room temperature and its contents analyzed using gas chromatography no ammonia was detected. Careful examimation of the trap tubing revealed small droplets of water which had condensed between the purging vessel and the Chromosorb 103 trap. It was assumed, and later proved that the ammonia was being retained in the water droplets.

When the trap and connecting tubing was heated to 100°C before injection onto the gas chromatographic column, a 63% ammonia recovery was obtained. Attempts to remove the water after the sample was purged from the regeneration apparatus but before the Chromosorb 103 trap using various adsorbents proved to decrease the total amount of ammonia recovered. When calcium sulfate was tested for water removal the ammonia recovery fell to 15%. The use of 5A molecular sieves, preconditioned at 350°C under a helium purge, provided a 62% ammonia recovery. Another precolumn, previously reported (15) to remove water from ammonia before analysis, is barium oxide. This material was not evaluated to determine ammonia recovery due to lack of availability.

Because of the problems associated with trapping ammonia in the conventional manner, a modified approach was attempted. Using the same regeneration flask shown in Figure 4-3, an aliquot of the acidic impinger solution was neutralized with sodium hydroxide. The heating mantel was then placed around the flask to heat the contents to boiling while nitrogen was purged through the solution. Ammonia and water vapors were condensed into an ice cooled microtrap (Figure 4-6) until approximately 250 microliters of condensate were collected. If 25 milliliters of impinger solution are used in the regeneration flask an effective concentration factor of 100 to 1 is achieved. A portion of this condensate is then analyzed using gas chroma-

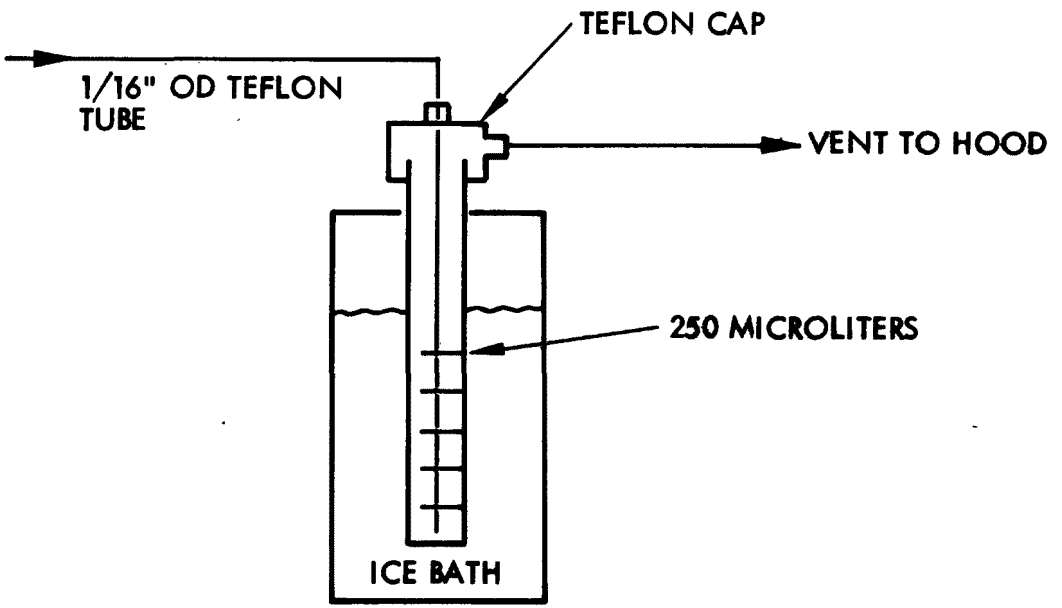


FIGURE 4-6 Ammonia Distillation Collector for Impinger Trapped Samples

tographic procedures. Using this stream distillation technique, 88% recovery for ammonia was obtained. Using the same technique, 97% of dimethylamine was recovered.

When a stream with relatively few impurities is sampled, the impinger solution can be analyzed for ammonia by direct titration, however when other basic materials are present in the effluent stream, which is most commonly the case, analysis of the ammonia is best accomplished using gas chromatography. Several columns were evaluated for the determination of ammonia, some of which are given in Table 4-4. The best column both in terms of convience as well as performance was found to be Chromosorb 103. This packing elutes ammonia and most low molecular weight amines without excessive tailing, and water does not effect the column material or interfere with the analysis of ammonia. The results reported for ammonia recovery as a part of this report were obtained using Chromosorb 103 and a micro-thermoconductivity detector. Thermoconductivity detectors are only moderately sensitive and very low concentrations of ammonia cannot be determined. Very few GC detectors have a good response for ammonia and none of these are in wide spread.

Analysis of Solid Adsorbent Obtained Samples for Basic Reduced Inorganic Gases --

If an adsorbent material is used to collect the basic inorganic gases, it is best analyzed directly using gas chromatography and thermoconductivity detection, as previously discussed. This approach will undoubtedly result in GC peak broadening however it is expected that the concentration will be relatively high if solid adsorbent sampling techniques were used. In application, a small adsorbent trap is used for sampling. After a known amount of the effluent stream has been sampled, the trap is connected to the front of the gas chromatographic column. The helium flow is started and the column programmed in temperature normally. It is expected that this technique will result in low recoveries due to losses during sample handling and irreproducable results due to inaccurate measurement of the ammonia peak area.

Analysis of Grab Samples for Basic Reduced Inorganic Gases --

Because of the moisture condensation problem previously discussed

Table 4-4

Effectiveness of Columns for Amine Analysis

Column	Comments
15% Diglycerol + 5% TEP on Chrom W	Did not separate DMA from TMA at µg concentration. Excessive bleed.
Chromosorb 103 Porous Polymer	Separates most amines and NH_3 without tailing, water does not interfere.
2% TEP on Graphite	Poor resolution.
4% Carbowax 20 M + 0.8% KOH on Carbopack B	Good but requires care in its use.
3% Poly-Al03 on Gas Chrom Q	Poor resolution.
Penwalt 223 on glass beads	Some tailing.
10% Amine 220 + 10% KOH on Chromosorb W	Effective at all concentrations.
Porapak Q treated with KOH	Column good but requires care in use
Porapak Q + 10% TEPA	Column good but requires care in use

(Section 4.2.1) and the subsequent loss of ammonia by solution in this condensed vapor, grab sample analysis can prove very difficult. The best technique, if grab samples are required, is to purge the grab sample into a mildly acidic impinger and then wash the interior portion of the grab container with a mild acid and add this washing to the impinger contents. The analysis for ammonia is then accomplished using the same procedures as outlined for impinger solution analysis above. It is not recommended that grab samples be used for the determination of basic reduced inorganic gases due to the obvious losses inherent with the technique.

Field Verification of The Impinger Sampling Procedure for Ammonia --

The field verification sampling for ammonia was conducted at the Paraho Shale Oil Demonstration Plant. The samples were taken using four impingers in series. The first impinger contained 20 ml of distilled water. The second and third impingers contained 5% HCl and the fourth contained silica gel to dry the gas stream. The analysis for ammonia collected using this impinger system was accomplished by titration (22), due to the high ammonia concentration and lack of interferences. The results of the test are given in Table 4-5. The ammonia levels were expectantly high from the conversion process. The sampling points and a descreption of the plant are given in Section 4.3.1. The samples exhibited good reproductability and show that the level of ammonia varies with time.

Table 4-5

Ammonia Analysis Results from Paraho Shale Oil Facility

Date	Test	Volume of Gas (M^3)	NH_3 Detected (PPM)
9/77	NH_3-1	.06	13,000
9/77	NH_3-2	.05	18,000
9/77	NH_3-3	.02	15,000
10/77	NH_3-1	.08	5,000
10/77	NH_3-2	.08	7,000
10/77	NH_3-3	.09	6,000
10/77	NH_3-4	.08	7,000

4.3 SAMPLING AND ANALYSIS OF "NEUTRAL" REDUCED INORGANIC GASES

The term "neutral" reduced inorganic gases is used for those species which show little affinity to accept or donote a H^+ in aqueous solution. The sampling and analysis of these species is based on molecular characteristics other than their affinity for acids or bases. Such compounds as $(CN)_2$, COS and AsH_3 exhibit these characteristics as well as metals such as mercury and selenium.

In most cases the elements and compounds studied are unstable and must be sampled in a way that chemically alters their structure to provide inhanced stability. As will be discussed below, this inherent reactivity is used in most cases as the basis for sampling and analysis. General purpose sampling equipment is for the most part not applicable to these compounds and specialized sampling and analysis techniques must be used to effect quantitative determination at low concentrations.

4.3.1 Sampling and Analysis of Selected Metal Hydrides (PH_3, AsH_3 and SbH_3)

The methods discussed in this section are designed to sample and analyze for arsenic in its reduced forms such as arsine, methylarsine, and other organometallic arsine compounds. In addition, stibine and its organometallic forms and phosphine and its organometallic forms can be determined. The method is designed to provide for sampling of these gaseous species at the trace level and to perform analysis remote from the emission source. Traditional methods for the determination of the metals include atomic absorption and spark source mass spectrometry, however these techniques only determine total metal and do not determine the type of compounds in which they may be found.

The sampling and analysis of reactive gases at low levels is a challange, without instrumentation at the source. The trapping of gases for remote analysis generally results in significant compound modification. Armed with these facts, the methods presented here take advantage of the chemistry of the compounds. The gases are chemically modified for stability and then transported to the laboratory for analysis. All reduced compounds of arsenic, antimony, and phosphorus are determined in a single sampling thereby lowering the cost for both sampling and analysis.

Previous work by Braman and co-workers (16,17) has resulted in procedures for the determination arsenic oxidation states. Braman's techniques involve the reduction of arsenic compounds using sodium borohydride at specific solution pH resulting in their sequential gaseous evolution. The arsenic oxidation states are determined by the pH at which the reduction and subsequent evolution takes place. The reduction chemistry of Braman's method is shown in Figure 4-7. The pH of the solution in which the reduction takes place is very important since the various arsenic acids must be in their completely protonated state before reduction can proceed. As an example; arsenous acid (pKa = 9.23) can be reduced at a pH of 4-5. At this pH arsenic acid (pKa = 2.35) will not be reduced and arsenic (III) can be determined in the presence of arsenic (V). After the arsenic (III) is evolved the solution pH can be lowered and the arsenic (V) reduced and determined. Braman used the difference in boiling points of the organoarsenic compounds to provide for their separation and determination. It has been suggested that antimony compounds could be determined in much the same way (17).

The hydrides (phosphine, arsine, and stibine) can be formed in several commercial processes, such as in a reducing acidic atmosphere where the element is present (e.g., coal gasification or liquifaction) and by several electrolytic processes. The stability of the hydrides is marginal decreasing in the order $PH_3 > AsH_3 >> SbH_3$, so that stibine is very unstable, thermally decomposing instantly to the metal under mild heat or even at room temperature in only a few hours. Sampling techniques for the hydrides which take advantage of their strong reducing character were investigated as candidate methods. The expected low concentration of these compounds in a typical source emission dictates micro techniques be used so that subsequent analysis can be performed without excessive preconcentration. The following discussion presents the chemistry of the hydrides as well as sampling and analysis procedures developed for their determination.

Chemistry of Selected Hydrides (PH_3, AsH_3, and SbH_3) --

PH_3 (Phosphine)

Phosphine, the most stable of the hydrides discussed, is not spontaneously flammable but is readily oxidized by air upon ignition. The compound is exceedingly poisonous, sparingly soluble in water, and is a strong reducing

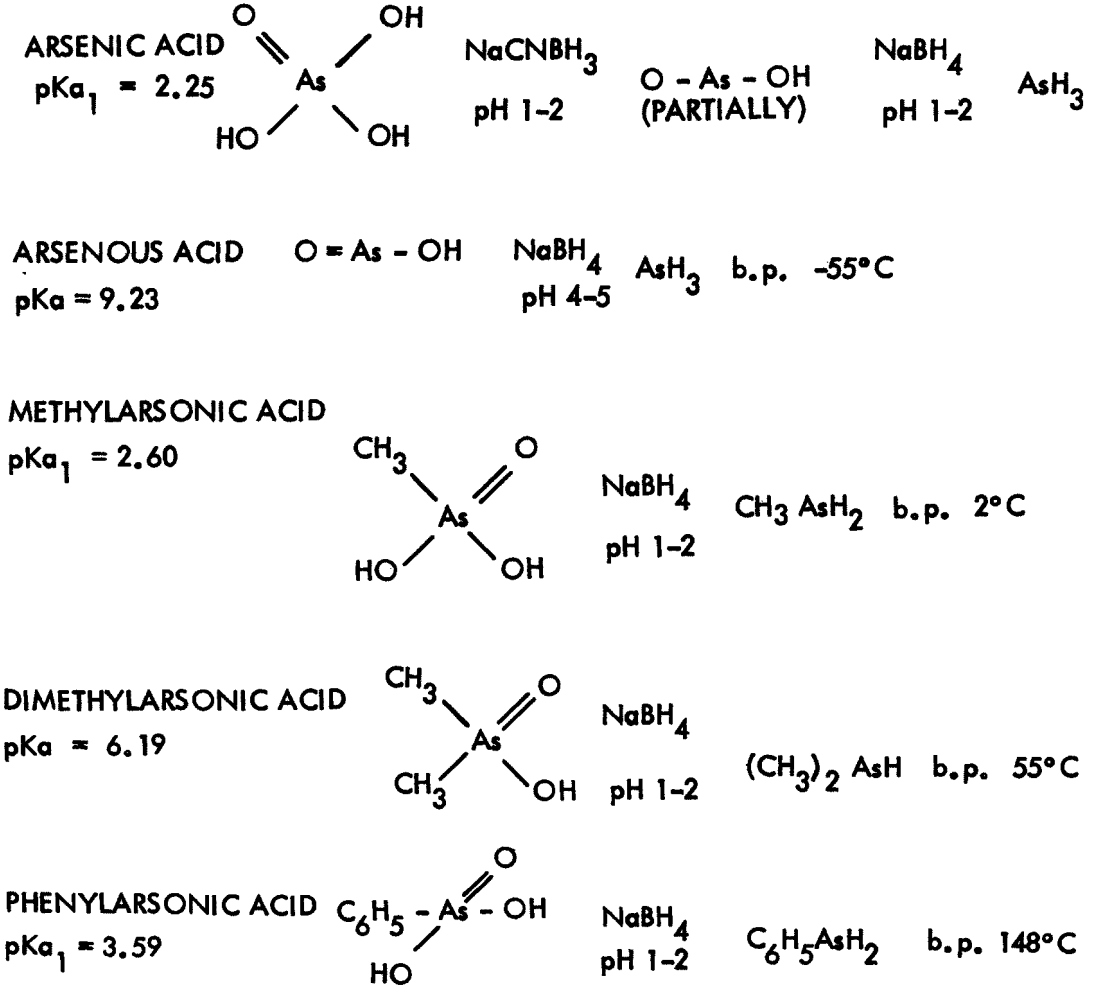


FIGURE 4-7 Reduction Chemistry of Arsenic Acids

agent.

Phosphine is generated by the direct reaction of elemental phosphorus with hydrogen at elevated temperatures (>300°C), increased pressure of hydrogen tends to yield much greater quantites of the gas. Diphosphine is often produced at a low level when PH_3 is generated, and is pyrophoric. Phosphine is sparingly soluble in water and shows only a slight tendency to produce the phosphonous ion PH_4^+. When formed it is very unstable and could not be determined in a "real" sample.

AsH_3 (Arsine)

Arsine is extremely poisonous and is readily decomposed thermally to arsenic metal, which is deposited on hot surfaces as a minor. The decomposition temperature of arsine to arsenic is quoted to be 300°C. However in the presence of metal surfaces or impurities, the reaction can take place at much lower temperatures. Arsine is a more powerful reducing agent than phosphine and is converted on oxidation to arsenous acid in aqueous solution or arsenic trioxide in air.

Arsine is not formed by direct reaction of arsenic metal with elemental hydrogen since the temperatures required for this reaction cause decomposition. Under conditions of high hydrogen pressure, or by catalysis arsine can be formed. Arsine is, however formed by electrolytic reaction and in those industries where such processes occur and arsenic is present arsine may be evolved. It has also been observed that specific strains of bacteria or fungi can convert organoarsenic compounds to arsine at a level which is harmful to animal life.

SbH_3 (Stibine)

Stibine has a high degree of thermal instability, at 200°C stibine is very rapidly decomposed and will be deposited as metallic antimony. Due to its thermal instability stibine tends to be formed in those processes where electrolytic or catalytic reactions are performed. Metal refineries where water comes in contact with hot antimony containing materials (aluminum catalyzes this reaction) tend to produce stibine. It is also generated when batteries contaminated with antimony are charged. Stibine decomposes even at room temperature, so hazards associated with exposure are usually related to close work or confined areas.

Sampling for The Hydrides --

Due to the strong reducing nature of compounds such as phosphine, arsine, and stibine, it was determined that an oxidative impinger would be the best means for sampling the materials in a gaseous stream. Immediately on contact with a strong (or even mild) oxidizer, the hydrides react. In an aqueous solution the hydrides are converted to their respective acids (e.g., arsine is converted to a mixture of arsenous and arsenic acids). Some assumptions must be made before this sampling technique is used. The most important of these is that the stream being sampled is indeed reducing. The assumption of a reducing stream must be made since the oxidized forms of the elements will be determined as their respective reduced forms by this procedure.

The sampling method recommended as a result of this work, utilizes an oxidative impinger train containing 30% hydrogen peroxide. The gases from the reduced stream are pulled through the impingers using a small vacuum pump until a volume consistent with detection requirements, has been sampled.

Blanks are very important for the subsequent analysis. Depending on the type of detection system used, artifacts from the reagents used can adversly affect results. By analyzing blanks these interferences will at least be noted and in most cases can be removed.

Under laboratory conditions, more than 90% of the arsine generated in a reaction vessel can be trapped in a single midget impinger filled with 30% H_2O_2. Less than 2% of the generated arsine appears in a second impinger connected in series. Some arsine probably remains in the reaction vessel or decomposes in transit to the first impinger.

Analysis of The Hydrides --

The method developed for the determination of the hydrides (PH_3, AsH_3, and SbH_3) requires, the use of GC/MS for separation and determination. The procedure, as described, was verified in the laboratory using standards prior to a field evaluation.

Samples obtained using the hydrogen peroxide impingers previously discussed must first be treated to destroy the H_2O_2. The destruction

procedure involves making the peroxide solution basic and refluxing for 1 to 2 hours. The peroxide destruction is necessary since the subsequent analysis requires reduction of the arsenic compounds in this impinger solution. The degree of distruction of the hydrogen peroxide can be measured by taking a small amount of the sample and adding it to a solution of potassium iodide. If the solution remains colorless, the peroxide destruction is complete. If the solution yellows, the destruction is incomplete and a judgement has to be made as to whether the solution should be refluxed longer or more reducing reagent added when the analysis is performed.

Figure 4-8 shows the reduced gas generation apparatus which was used for generating the hydride sample gas. For analysis, the sample is aliquoted into the generation cell, shown at the left of Figure 4-8. An excess of oxalic acid is added to reduce the solution pH followed by sodium borohydride. The system is purged with helium and the gas passed through a Drierite trap to remove moisture. Moisture removal is required to avoid plugging of the liquid nitrogen trap with ice. The sample is condensed by the LN_2 and the trap isolated after reduction and purging is complete.

All connecting lines to the GC/MS must be non-metallic to avoid sample degradation. The presence of any metal in the system will result in very low recovery for the hydrides. It was necessary for this technique to work, to remove the GC injector block and connect the trap directly to the glass column in the gas chromatograph. Once generated, the reduced gases are stable for 1 to 3 hours. If analysis is performed during this period, no significant sample degradation was observed. Samples allowed to stand overnight after being reduced to their gaseous forms, even in the inert helium atmosphere used to purge the generation cell, decompose completely to their respective metals. After generation, the sample trap is allowed to warm, the valves opened, and the gaseous sample injected by flushing with carrier gas onto the GC column.

During the initial phases of this work, the mass spectrometer was scanned over a mass range which allowed for the determination of all the compounds of interest. Subsequent analysis have been accomplished with higher sensitivity by monitoring narrow ranges of the mass spectrum where the molecular ions of the species of interest predominate. The chromatography

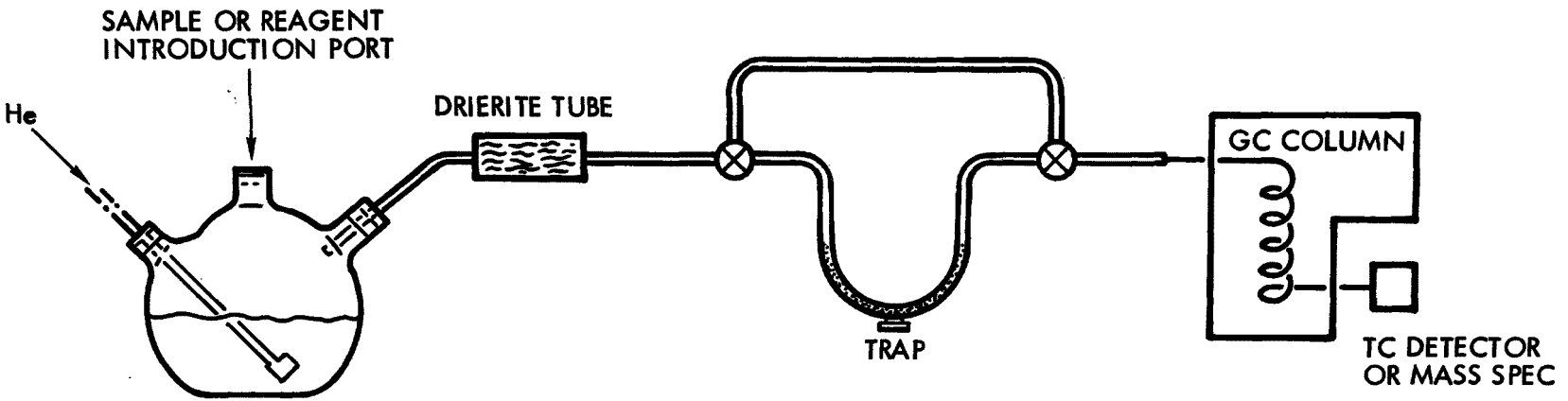


FIGURE 4-8 Reduced Gas Evolution Apparatus

was accomplished using a Carbowax column and the conditions given below:

- Column type: glass, 10% Carbowax 20M on Chromosorb 101, 100/120 mesh.
- Column length: 1 meter X 2 mm I.D.
- Flow rate: 20 cc/min (helium)
- Temperature program: 50°C for 1.5 min, 50°C - 100°C at 6°C/min
- No injector was used for these analysis and the sample loop was allowed to warm to room temperature (5 min) before analysis. For less volatile organometallics, the loop was gently heated.

Figure 4-9 shows a reconstructed gas chromatogram of a mixture of phosphine, arsine, stibine, and methylarsine. This chromatogram resulted from a synthetic mixture produced by dissolving phosphoric acid, antimony trioxide, arsenous acid, and methylarsenoic acid in water and reducing using the procedure previously described. As can be seen the chromatography allows for the separation of all components. The only interference occurs with the coelution of phosphine and air. Figure 4-10 illustrates this coelution by displaying the molecular ion of phosphine (M/e = 34), plotted on the same scale as the molecular ion for oxygen (M/e = 32), relative to scan number. This interference was significant and could prohibit the determination of phosphine on this GC column. Other work has shown that this interference can be eliminated by using a 4A molecular sieve column for the specific determination of phosphine. Figure 4-11 shows the spectrum of phosphine with the interference from air being quite obvious.

Also on the Carbowax column, stibine coelutes with water, the amount of water in the sample is a direct function of the age of the Drierite used in the trap during the regeneration process. It was found that the coelution of stibine and water did not adversely effect the determination of stibine even at low concentrations. Figure 4-12 shows the spectrum of stibine with its molecular ion at M/e = 124 and its antimony isotope pattern. Arsine elutes in a very clean region of the chromatogram with no interferences. The spectrum for arsine is shown for reference in Figure 4-13 and has a molecular ion at mass 78. Arsine is monoisotopic and therefor has no isotope pattern. Arsine shows only trival fragmentation with the loss of hydrogen from the molecular ion as the main fragmentation process. Finally the mass spectrum of methylarsine, molecular weight 92, is given in Figure 4-14 showing it to be similar to arsine except that the loss of methane is

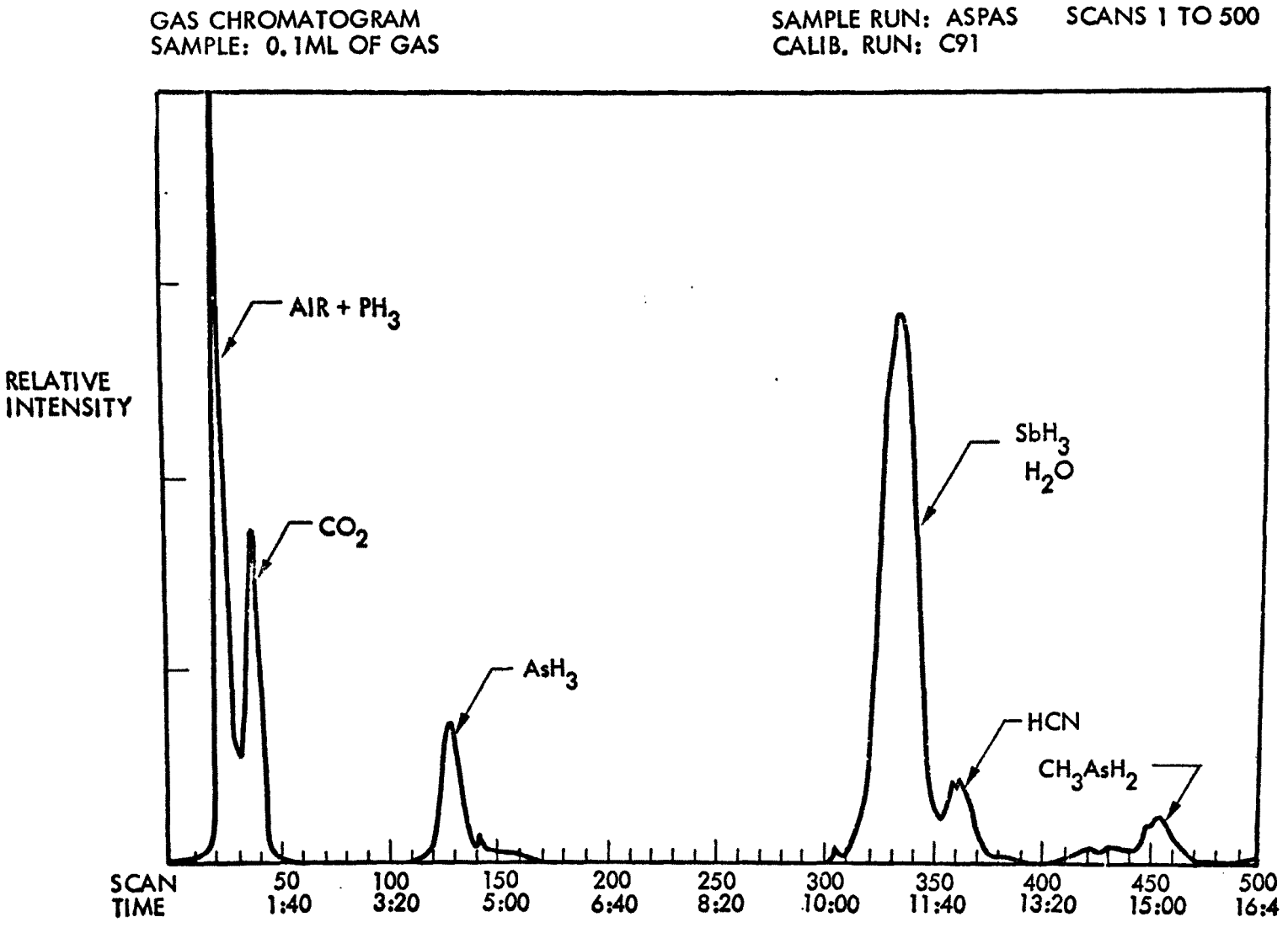


FIGURE 4-9 Resconstructed Gas Chromatogram of The Hydrides Produced by Reduction Procedure

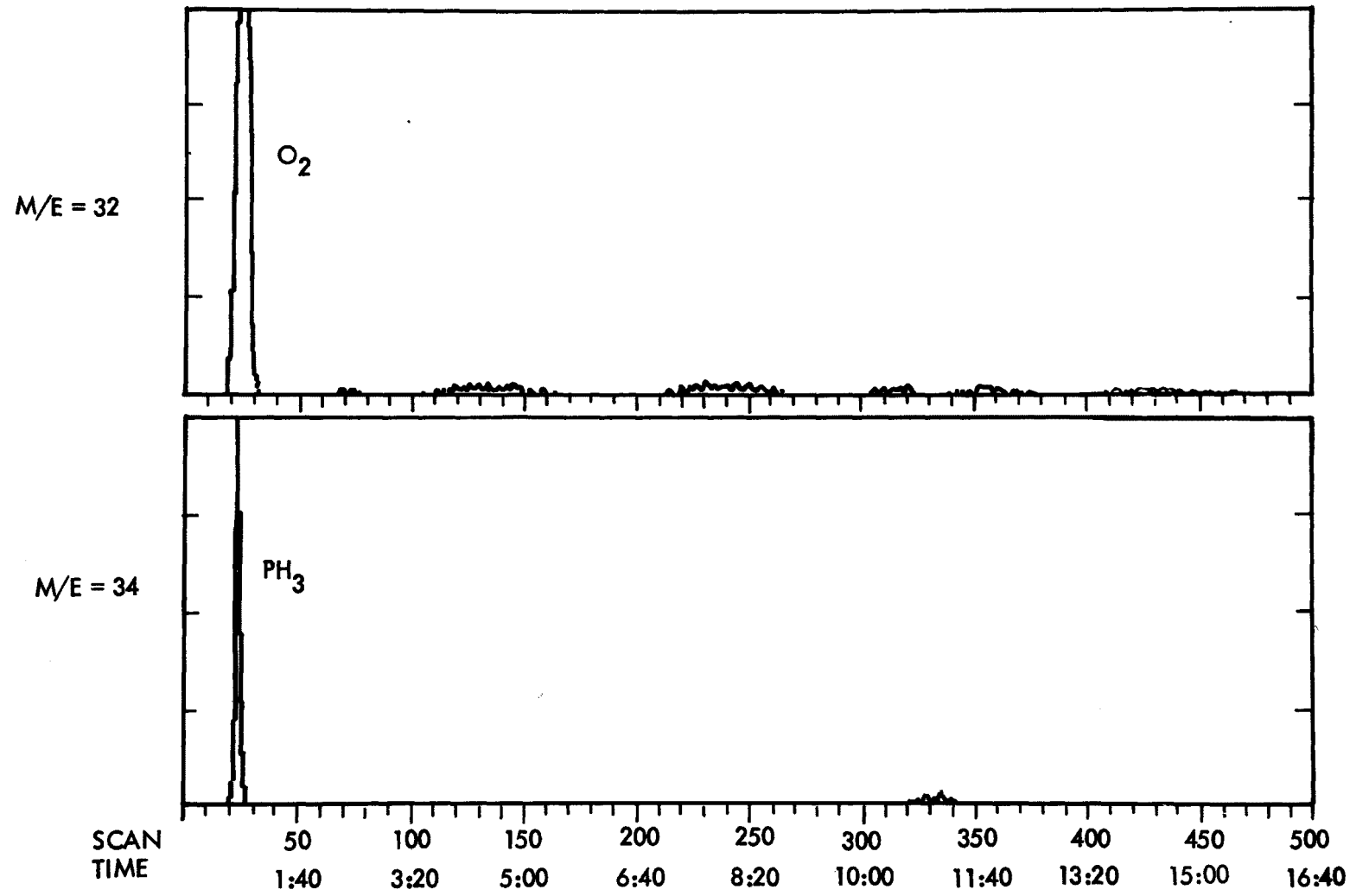


FIGURE 4-10 Mass Chromatograms for Oxygen (M/e=32) and Phosphine (M/e=34) Showing Coelution

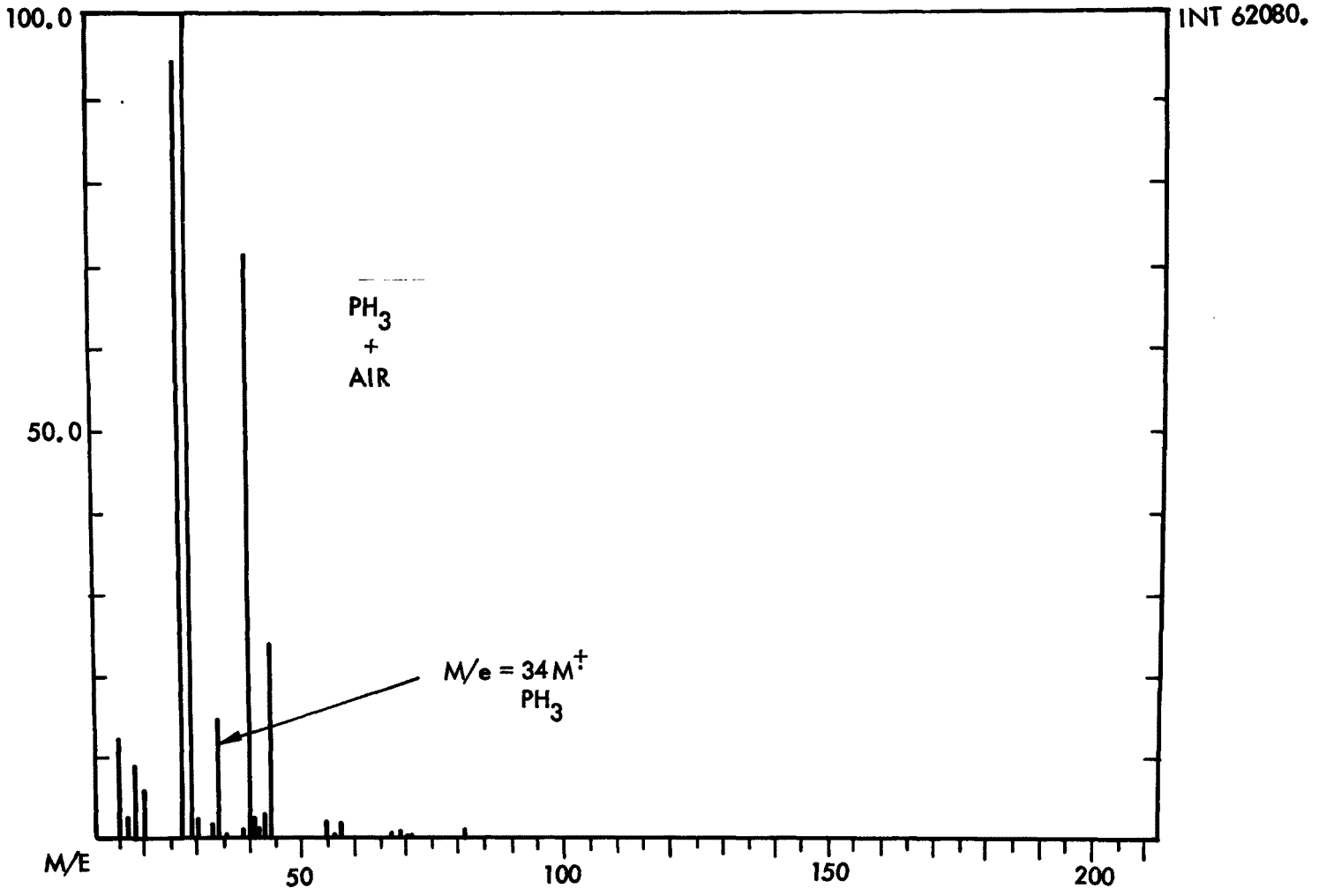


FIGURE 4-11 Mass Spectrum of Phosphine and Air (Scan 22)

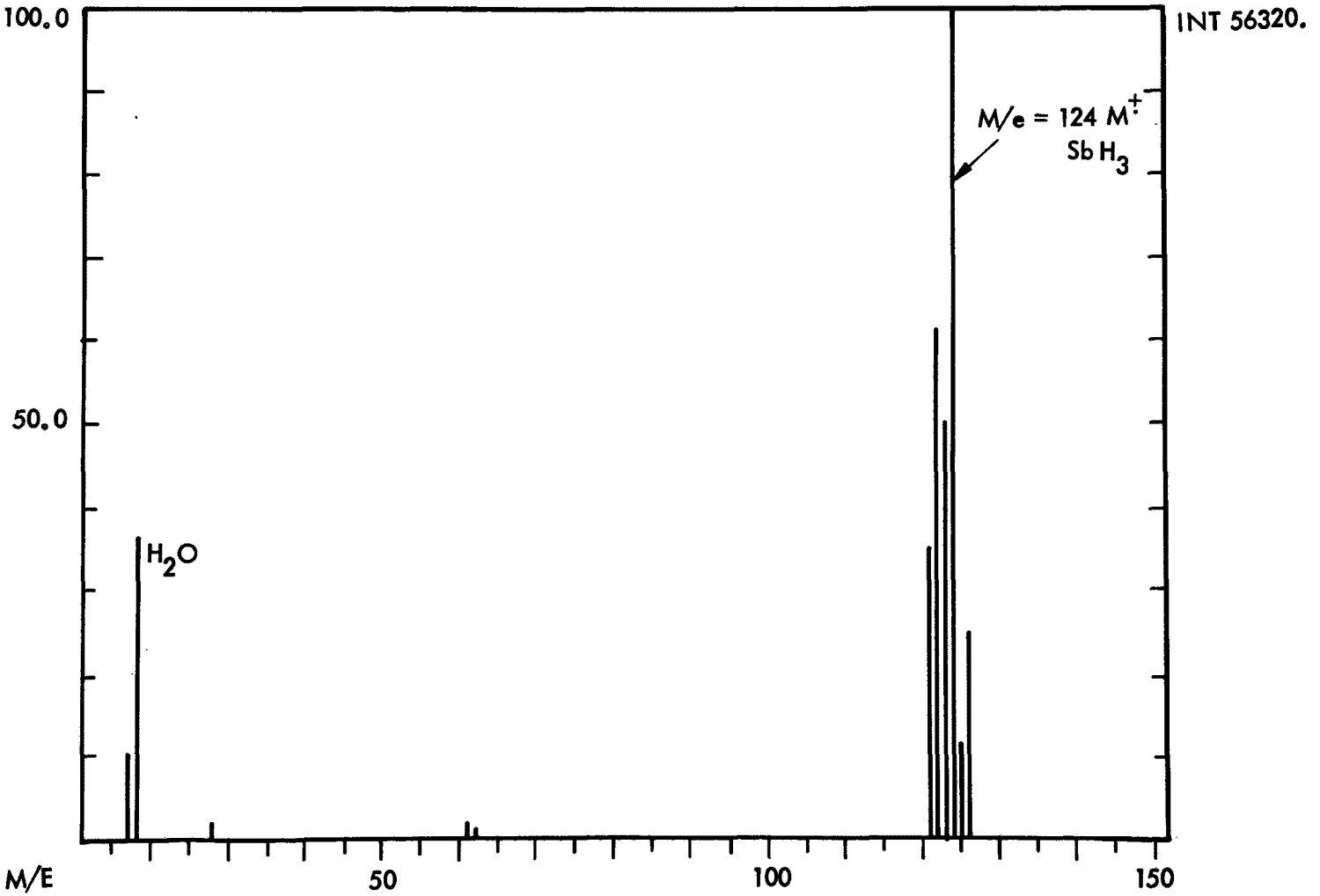


FIGURE 4-12 Mass Spectrum of Stibine (Scan 325)

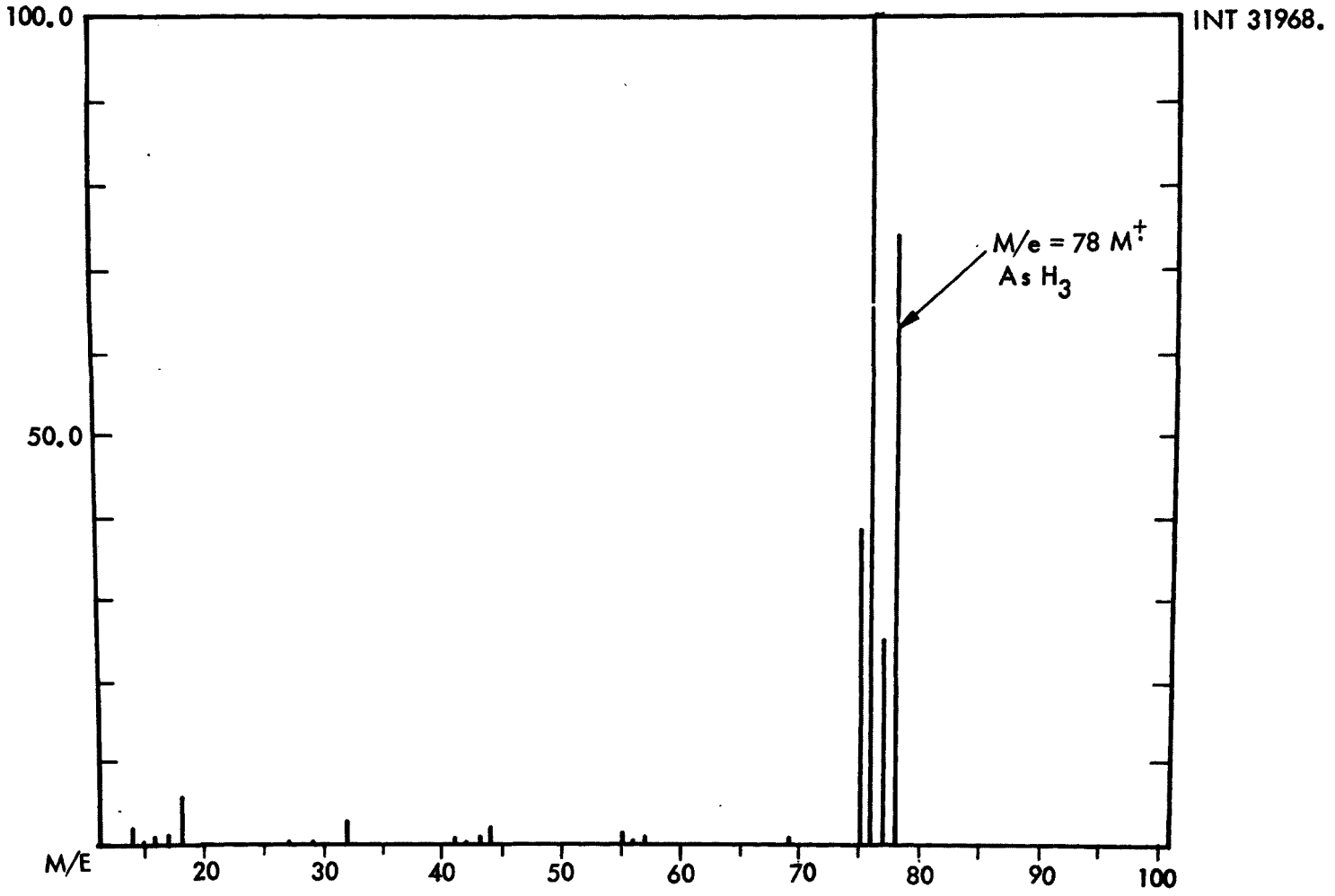


FIGURE 4-13 Mass Spectrum of Arsine (Scan 128)

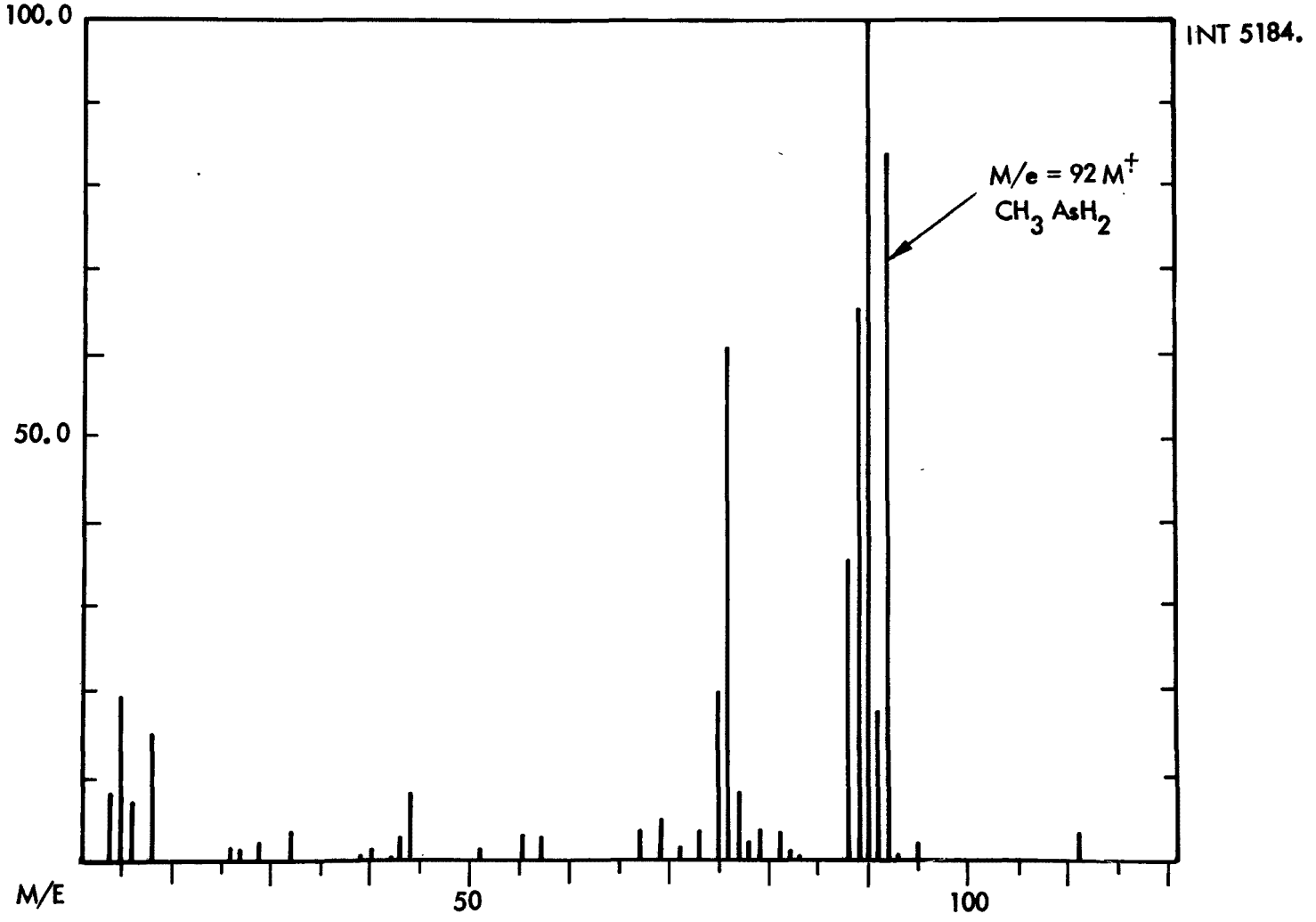


FIGURE 4-14 Mass Spectrum of Methyl Arsine (Scan 454)

observed from the molecular ion.

Figure 4-15 shows the mass spectrometer response to arsine as a function of concentration in order to determine the linearity of the instrument to this reduced gas. The curve was generated by adding known amounts of arsenous acid to the previously described reduction vessel and producing known accounts of arsine. As can be seen, the response is linear from about 50 nanograms of arsine injected to about 500 nanograms. A knowledge of the linear response range permits the analyst to adjust the amount of material in the generation vessel by using smaller or larger aliquots of the sample. Similarily, the response for stibine is shown in Figure 4-16 with essentially the same linear working region. Analysis should be performed only within this linear region and the curve should be generated for each mass spectrometer system used since the linear response of each instrument will be different.

The use of a mass spectrometer as a detector for this analysis can only be described as "overkill". Less expensive systems need to be investigated. A second draw back to the GC/MS system is that the metallic hydrides decompose in the mass spectrometer ion source producing conductive paths. These conductive paths cause the mass spectrometer to become non-functional in a very short period of time and increase the frequency of ion source cleaning.

As a part of this program the use of alternative detectors has been studied. A thermoconductivity detector (TC) is a good general purpose GC detector which responds to the hydrides. The TC detector however, lacks sufficient sensitivity and specificity to be useful. The thermionic detector (N/P) was evaluated as a possible alternative to mass spectrometry however it was found not to respond to any of the hydrides, including ammonia. A third detection system (not evaluated) is flame photometric detection. It is anticipated that with the use of selective filters this detector may prove to be the most practical. The flame photometric detector has the inherent sensitivity and with proper filters should also have good selectivity. It is doubtful that one could devise a flame photometric detection system which would allow for complete analysis of all hydrides in one chromatographic run since filter selection would be based on a specific element. Other possible detection systems include micro wave discharge, spectral emission and atomic absorption but the higher costs of these systems makes them less

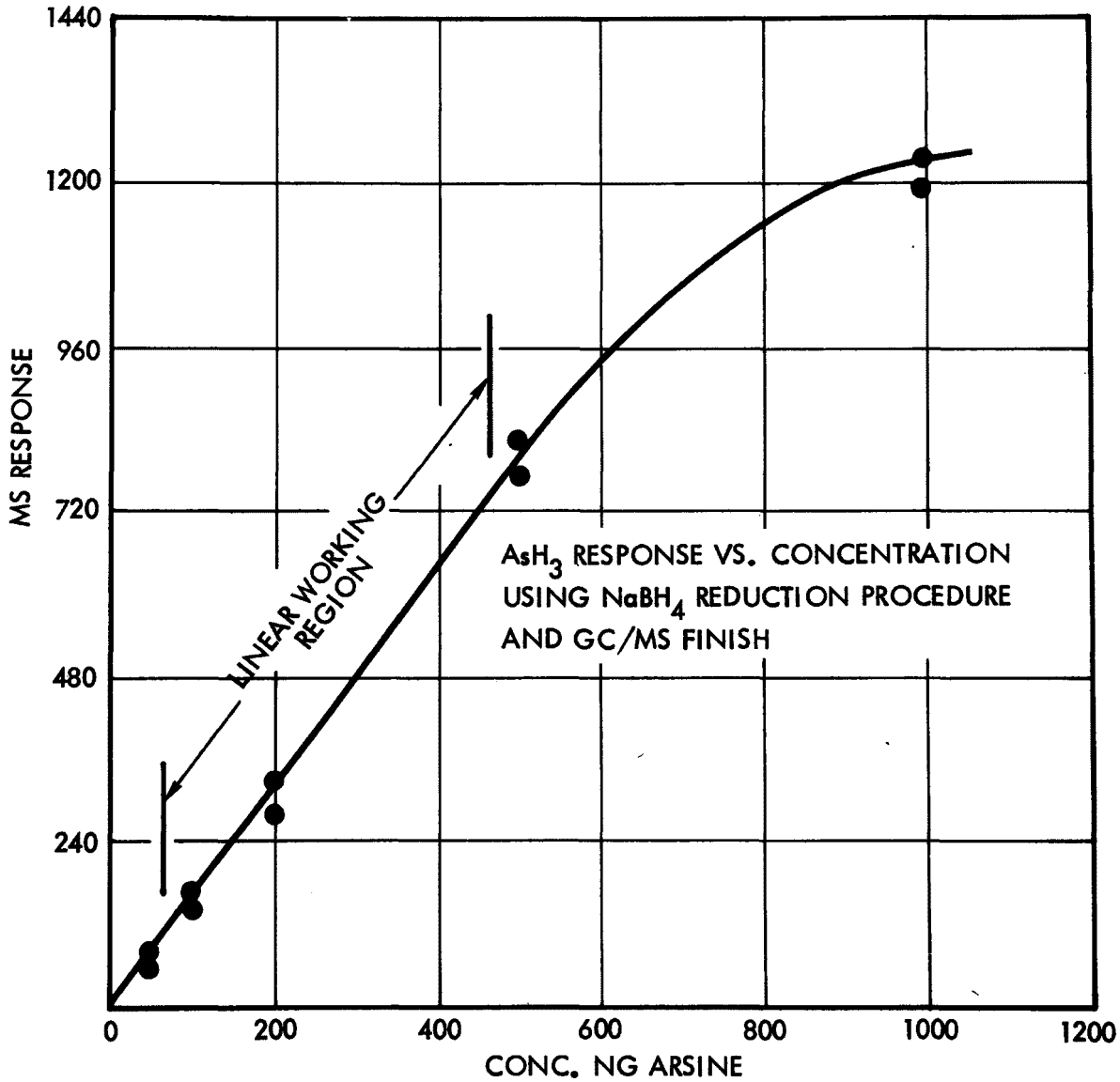


FIGURE 4-15 Arsine Calibration Curve

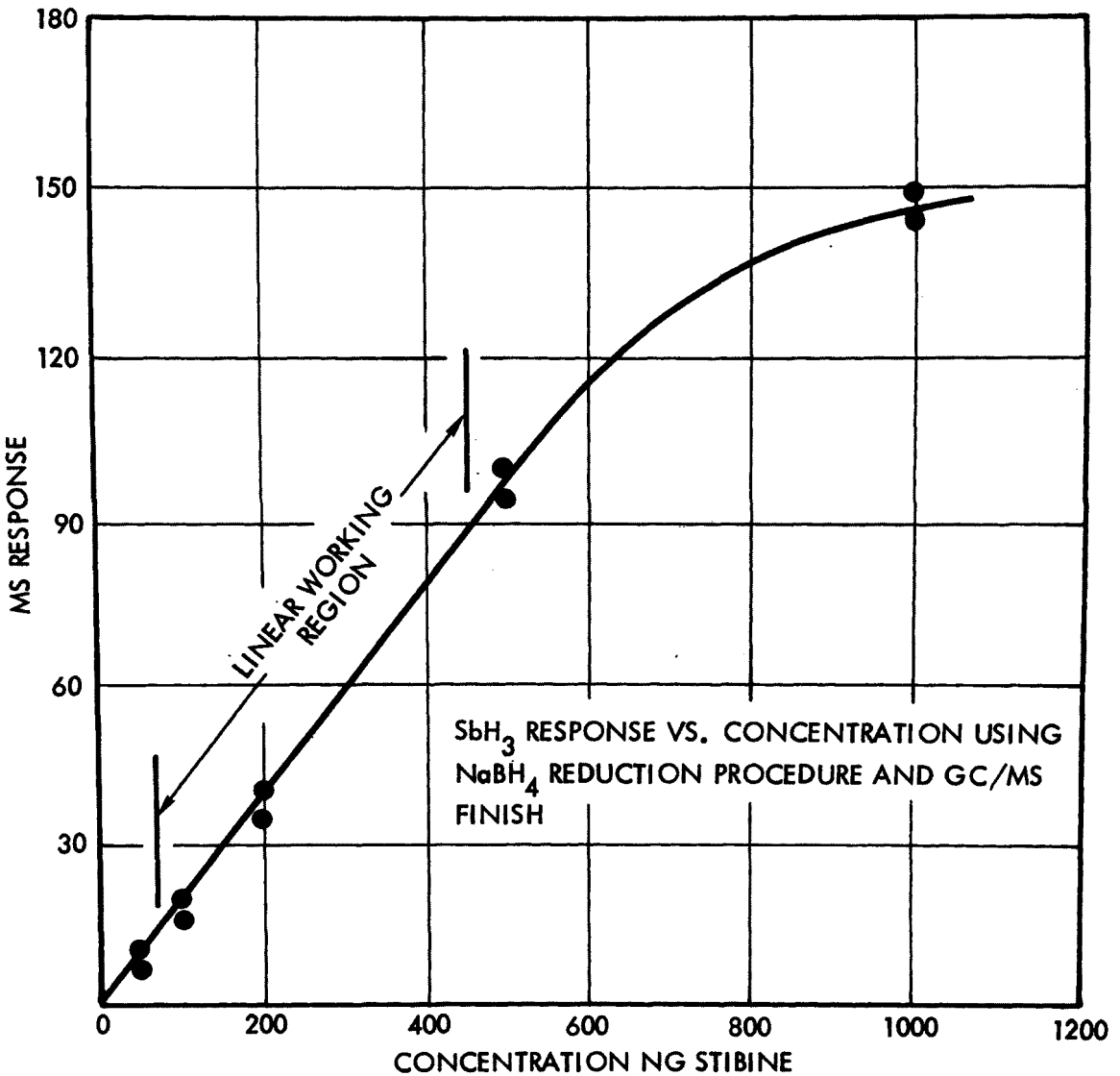


FIGURE 4-16 Stibine Calibration Curve

practical.

Field Verification of Hydride Procedures --

A field test of the sampling and analysis procedures for the hydrides was conducted at the Paraho Shale Oil Demonstration Plant. The Paraho semiworks retort uses the same system configuration for solid and gas handling as a full-scale plant. The retort is capable of being operated in either a direct or indirect heating mode at mass feed rates of up to 200 $Kg/hr/M^2$.

During the period of this test the retort was operated in the direct mode (gas combustion) only. In this mode of operation the carbon on the retorted shale is burned in the combustion zone (see Figure 4-17) to provide the principle fuel for the process. The low calorie retort gases are recycled to both the combustion zone and the gas preheating zone. The portion of retort gas which is not recycled is sent to a thermal oxidizer for combustion.

In operation, raw shale is fed into the top of the retort and passed downward by gravity successively through a mist formation and preheating zone, a retorting zone, a combustion zone, and finally, a residue cooling and gas preheating zone. It is discharged through a hydraulically-operated grate, which controls the discharge rate and maintains even flow across the retort.

The oil vapors produced in the retorting zone are cooled to a stable mist by the incoming raw shale (which is thereby preheated), and exit the retort for collection. This mist is sent to a condenser, and finally a wet electrostatic precipitator, for oil separation.

Samples for arsine were taken from the recycle gas stream at a point between the electrostatic precipitator and the recycle gas blower (point A, Figure 4-17). This location was chosen because of the moderate pressure and temperature of the recycle gas. The moderate conditions allowed the sample to be drawn through the impingers without treatment since the gas is relatively free of oil mist.

The sample was drawn through 5 impingers in series. The first impinger was empty, impingers 2-4 contained 100 ml of 30% H_2O_2, and the last impinger contained 200 g of silica gel. The impinger solutions were combined in

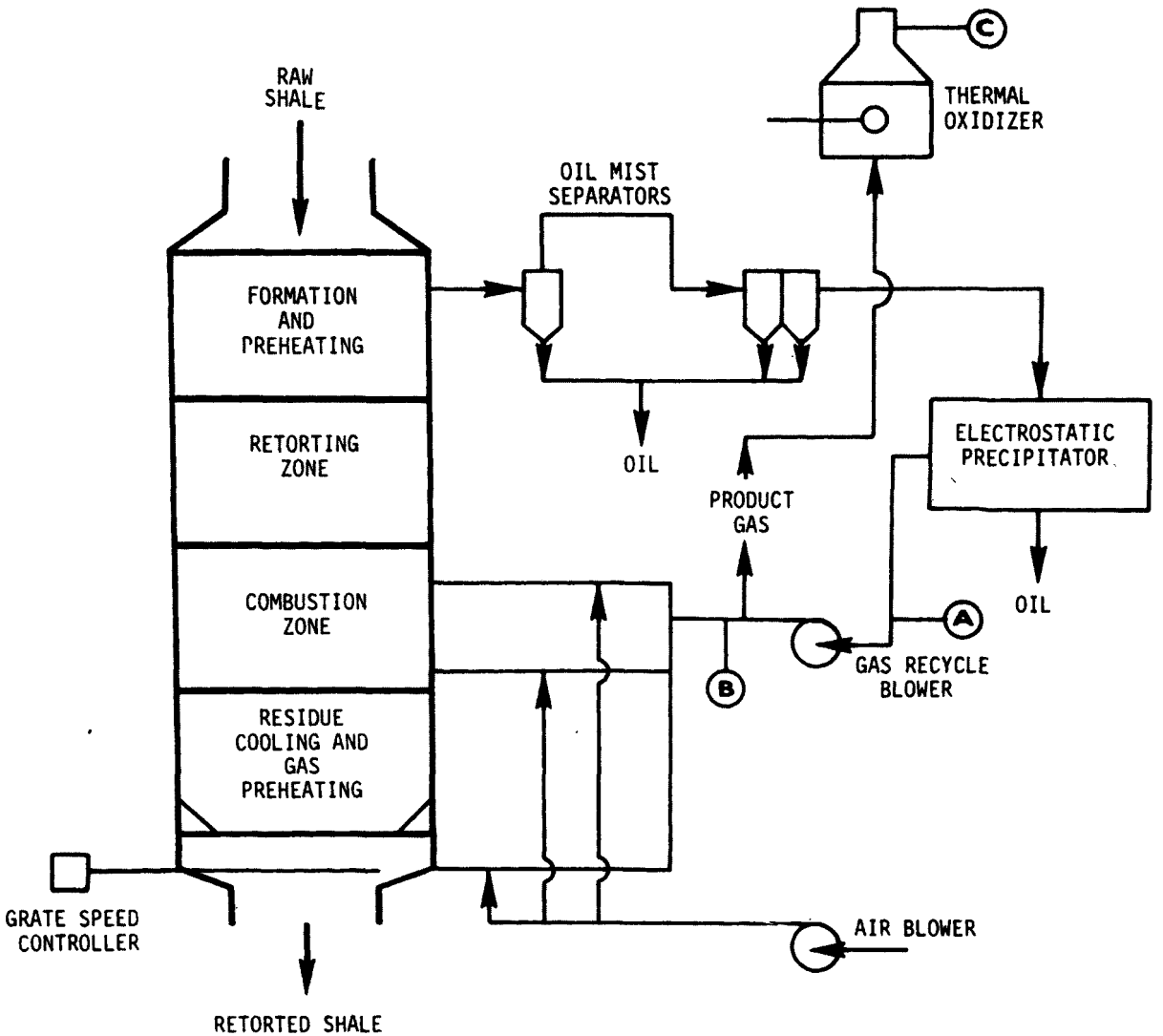


FIGURE 4-17 Schematic of Paraho Retort

the field prior to transport to the laboratory for analysis.

A total of four individual samples were obtained from the recycle gas stream. These samples were analyzed in triplicate using the procedures previously described.

The results of the analyses are presented in Table 4-6.

Table 4-6

Field Test Results for Arsine

Sample No.	Volume Sampled	Amount Arsine Detected	$\mu g/M^3$ Arsine
1	0.15 M^3	.025 µg	0.17
2	0.14 M^3	.035 µg	0.25
3	0.13 M^3	.045 µg	0.35
4	0.13 M^3	.060 µg	0.46

Arsine was the only hydride detected in the samples analyzed and no organometallic species were detected. The results of triplicate analysis of the same sample were within ± 20% relative. The deviation of the amount of arsine found between samples is probably due to the small sample volumes obtained and the non-homogeneity of the recycle gas stream due to process variations.

4.3.2 Sampling and Analysis of The Volatile Elements (Hg and Se)

Volatile elements present special problems in sampling and analysis. The most significant of these problems is the difficulty in determining the exact structure of the compound or element emitted from a given source. Most analytical procedures have the ability to determine the amount of an element in a given stream but to state that it was emitted as the element or the oxide is very difficult. The following sections give some insight to this problem and suggests procedures to overcome the difficulty.

Sampling and Analysis For Mercury (Hg) --

Mercury is a health hazard due to absorption of nearly 80% of the inhaled vapor by the body at concentrations between 50 and 350 $\mu g/M^3$. Elemental and organic mercury compounds pose additional problems by being

absorbed through the skin. The toxicity of mercury is due to the strong bonds formed by it with sulfur atoms in body components which results in an interference in the various body functions including synthesis and function of both enzymes and proteins. Mercury is a cumulative poison and concentrates in the brain, liver, and other organs.

Mercury and its compounds, are quite prominent environmental pollutants from natural and manmade sources. Elemental mercury enters the atmosphere from such sources as active geothermal sites, ore deposits, mining operations, coal burning, and smelting operations. The most common forms of mercury in the environment include the metal, halides, oxides and organomercurials.

Atomic absorption spectrometry (AAS) is the most common analytical technique for the determination of mercury. In ideal cases it is capable of determining elemental mercury at concentrations as low as 15 ng/M^3 (18). The basic problem with AAS is its inability to distinguish the form in which the mercury is present. Until recently, no techniques were available for the specific determination of mercury compounds. The work of Braman and Johnson (19,20) has recently established a method for species identification of mercury and mercury compounds. The procedure utilizes sequential, selective absorption tubes for separation of specific mercury oxidation states and uses a DC discharge spectral emission detector for analysis. Using this method, analysis can be performed accurately on mercury concentrations as low as 0.1-0.5 ng/M^3 of air samples as small as 0.1 M^3.

In the procedure described by Braman, air samples are drawn through a connected series of 10 cm quartz tubes containing selective absorbents for the various chemical compounds of mercury. The first component of the sample collection apparatus is a glass fiber filter (Gelman Instrument Co. Type A) to retain particulate mercury. The volatile mercury species that pass this filter are collected in the quartz tubes that are shown in Figure 4-18. Also given in the figure is the function of each absorbant. The components of this selective sampling device are connected with 1.0 cm Teflon ^{R} sections. Air samples are drawn through the absorption tubes at about 1.5 l/min using a small diaphragm vacuum pump. Small quantities of water from air saturation are reported not to interfer, but corrections are required for temperature and the partial pressure of water in accordance

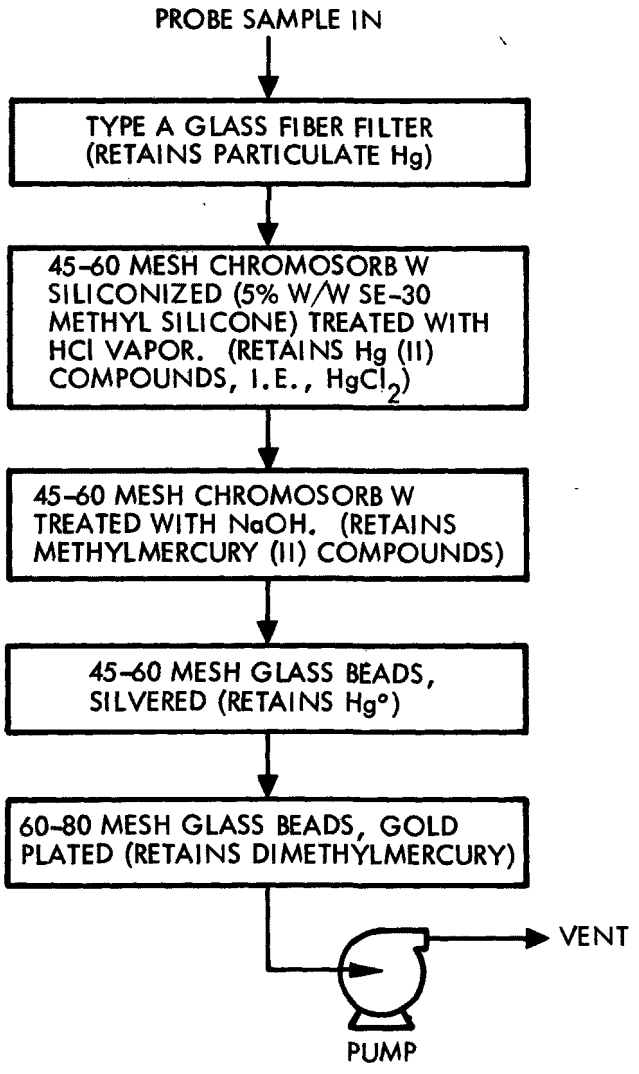


FIGURE 4-18 The Function of Selective Absorbers for The Sampling of Gaseous Mercury Compounds

with the standard ASTM test D 3195-73. The steps involved in the preparation of the substrates for each of the absorption tubes is presented in Tables 4-7 to 4-10.

As can be seen from the description of the Braman sampling device the separation of mercury compounds is achieved during the sampling process. In addition the samples collected in this manner are stabilized for transport to an off-site laboratory. The actual analysis of the mercury content of the selective absorption tubes can be accomplished by any of several techniques. The use of a DC discharge systems offers high sensitivity at modest cost, however AAS, electrochemical, or wet chemical techniques may also be used with various levels of sensitivity.

After air sampling is complete the sampling tubes are disassembled, sealed and sent to the laboratory. Once received they are treated to remove mercury or mercury compounds for analysis. If the DC discharge system is to be used the particulate filter is placed without handling directly into an empty Pyrex tube, of similar size to the sampling tubes. A heating coil is placed around the tube and it is attached directly to the DC discharge detector. After air is removed by passage of He carrier gas, the discharge is initiated and the tube heated rapidly to 550°C. Mercury compounds on the particulate filter are detected as a single peak during thermal desorption. No determination of compound type is possible in this portion of the sampling system. The Chromosorb W(HCl) and Chromosorb W(NaOH) absorption tubes are treated in a similar manner. The Chromosorb W(HCl) tube is heated to 250°C to remove the mercury (II) compounds (e.g., $HgCl_2$) and the Chromosorb W(NaOH) tube is heated to 300°C to remove the methyl mercury type compounds. All tubes must be blanked prior to use.

Calibration is made by using saturated mercury metal vapor in air. A gas-tight 0-0.5 ml syringe is used to sample the mercury vapor above a metal pool in a test tube fitted with a rubber septum. The test tube is kept in a water bath at room temperature measured to ± 1°C. Vapor pressure data are used to calculate the amount of mercury in the air delivered from the syringe.

This procedure was exaustively investigated by the authors and appears to be developed to the point that additional study is not required. With reasonable care, the method can analyze for mercury compounds as well as

Table 4-7

Preparation of Siliconized Chromosorb W (HCl)
For Mercury Sampling

- Pack 10-cm quartz tube to a length of 7 cm with Chromosorb W, 45-60 mesh.
- Add 60-70 milligrams of SE-30 to the top of the packed tube.
- Initiate a flow of helium carrier gas through tube.
- Slowly heat the tube with a wire coil heater until the SE-30 melts and is distributed onto Chromosorb W.
- Excess silicone is removed by heating the column for 10-20 min at 300°C with flow.
- Treat the Chromosorb W filled tube with 10cc of HCl vapors taken from the headspace of a bottle of concentrated HCl.
- Repeat HCl treatment after 8-10 uses.

Table 4-8

Preparation of NaOH Treated Chromosorb W
For Mercury Sampling

- Pack a 10 cm quartz tube to a 6-7 cm depth with Chromosorb W (45-60 mesh).
- Wet the Chromosorb W with 0.05N sodium hydroxide.
- Dry the material by passing carrier gas through column.
- Discard after failure during use.

Table 4-9

Preparation of Silvered Glass Beads
For Mercury Sampling

- Place 45-60 mesh glass beads in a container.
- Silver coat using the silver nitrate, ammonia, and formaldehyde silvering technique.
- Inspect peads under a microscope to determine that at least 90% are silvered (silver should be about 14% by weight on the beads).

Table 4-10

Preparation of Gold Coated Glass Beads
For Mercury Sampling

- Dissolve 12 grams of gold metal in aqua regia.
- Add concentrated HCl to remove the nitrates and convert the dissolved gold to auric chloride.
- Add 50 grams of HCl washed 45-60 mesh glass beads.
- Slowly evaporate, while stirring the auric chloride-glass bead mixture, to near dryness.
- Pack the semisolid mass into a 10 cm quartz tube, pass He or N_2 carrier gas through the tube and heat with a tube furnace.
- Add H_2 gas through a "T" in the carrier gas line as the tube is heated.
- After extended use heat the tube to 550-600°C while passing air to remove carbon or silicone deposits.

the metal in air at concentrations approaching 0.5 ng/M^3. The Braman approach should be considered as a standard sampling procedure when mercury compound identification from an emission source is required.

Sampling and Analysis for Selenium (Se) --

The levels of selenium and its compounds are of considerable interest as environmental pollutants. This interest is due to the toxic and potentially carcinogenic properties of selenium. Its natural abundance as well as the wide use of selenium or its compounds in manufacturing and industrial application, necessitate effective methods for measuring this element, especially at trace levels. Selenium can be found in many forms in the environment, including the metal, halides, oxides and organometallics.

Possible sources of trace selenium include natural fuels, leather goods, cloth materials, paper and other wood products. Coal has been found with as much as 7.4 ppm Se and significant amounts have been found in newsprint. The principal means of access to the environment is by incinerator stack emission where concentrations of 2 µg/M^3 have been determined.

Atomic absorption spectrometry (AAS) is the accepted analytical technique for the determination of selenium. In ideal cases the AAS is capable of determining elemental selenium at concentrations as low as 2 µg/M^3 based on a 30 M^3 sample. The basic problem with AAS is its inability to distinguish the form in which the selenium is present.

Sampling of effluent gas streams for selenium may be accomplished by the use of oxidative impingers such as H_2O_2 or absorbant filter paper wetted with strong cyanide solution. The purposed all glass sampling apparatus for selenium consists of a sampling probe through which the sample gas is drawn followed by a filter (recommended is the Gelman Instrument Co. Type glass fiber filter). The filter may either be placed in the filter holder directly or treated with cyanide solution before use. The criteria for using the filter with or without cyanide impregnation is based on particulate loading of the stream to be sampled. In the case of high particulate loading the filter should be used untreated to better handle the particulate catch.

In actual use, gas samples are pumped through a system of three impingers in series which are cooled by an ice bath. The first and second impingers

contain 750 milliliters of a 30% hydrogen peroxide solution and the third contains silica gel to protect the pump and dry test meter from moisture and possible reagent carry over. The recommended sampling apparatus is shown in Figure 4-19. After gas sampling is complete the filter is placed in a sealed petri dish and the impinger solutions are transferred into Nalgene bottles for return to the laboratory for analysis.

Selenium is determined in the samples by graphite furnace atomization AAS. The H_2O_2 impinger samples are treated with nickel nitrate solution until a concentration of 1% nickel is achieved. The nickel nitrate is used to convert the selenium to the selenide form during ashing in the graphite furnace. In this form the response for selenium is inhanced.

Particulate samples and filters are first digested using an HF-HNO_3 acid solution, then nickel nitrate is added to achieve a 1% solution prior to analysis by AAS. When the above techniques are used no compound identification is possible. At the present time no procedure appears adequate for compound identification of low selenium concentrations in effluent samples.

4.3.3 Sampling and Analysis of Miscellaneous Reduced Inorganic Gases

Two of the reduced gaseous inorganic compounds studied cannot be readily classified; these are cyanogen, $(CN)_2$, and carbonyl sulfide, COS. Cyanogen is very toxic (toxicity similar to HCN) and relatively stable at room temperature. At elevated temperature the compound tends to polymerize when maintained in the gaseous state. Carbonyl sulfide is also highly toxic and stable at room temperature. Carbonyl sulfide is soluble in water where it slowly decomposes to form carbonate and sulfide.

Sampling and analysis for COS and $(CN)_2$ is typically more conventional than some of the other reduced inorganic gases because of stability. Impinger and adsorbent sampling techniques hold the most promise for simple and rapid identification of the species. Gas chromatography is applicable for separation and analysis for both COS and $(CN)_2$.

Sampling for Carbonyl Sulfide and Cyanogen --

The traditional sampling procedure (21) for carbonyl sulfide involves

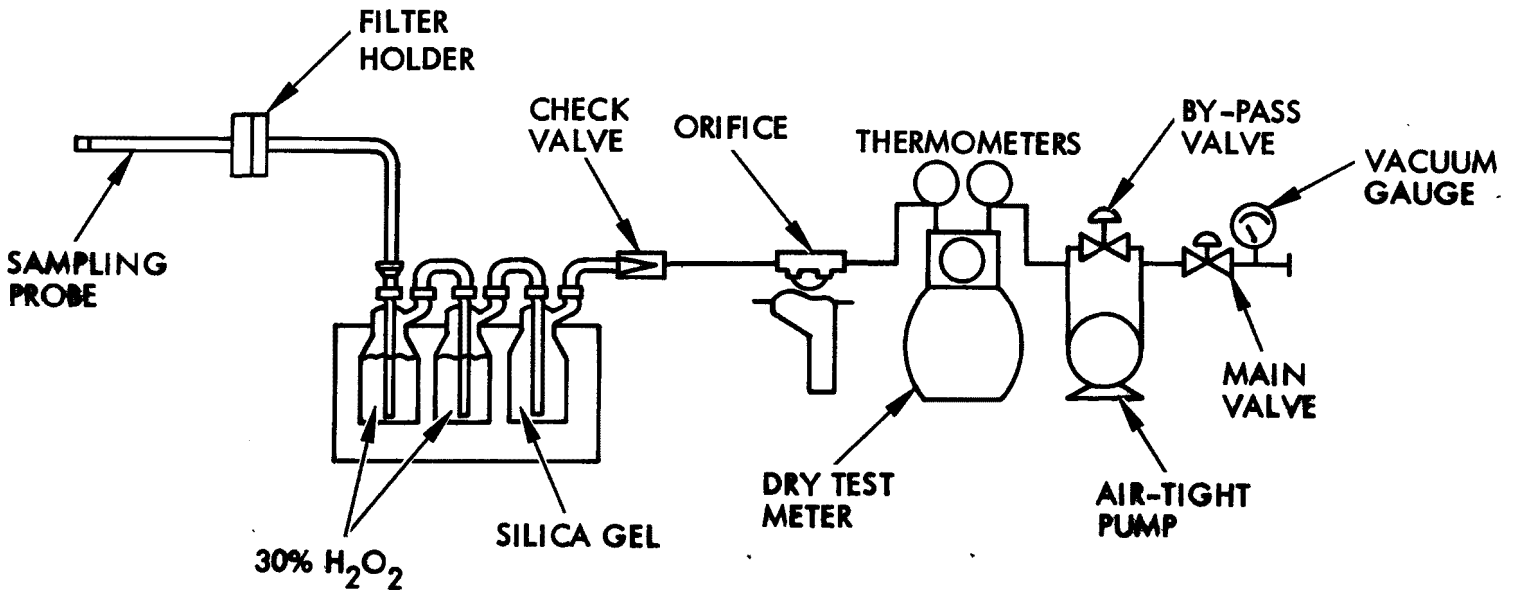


FIGURE 4-19 All Glass Sampling Apparatus for Selenium

the use of an impinger train containing calcium chloride and ammonium hydroxide for the selective removal of COS. Figure 4-20 illustrates this impinger train which was used for a field verification of the method. The first two impingers contain aqueous $Cd(OH)_2$ to remove H_2S which will interfere with the determination of COS if present. The third impinger is filled with an aqueous solution of $CaCl_2$ and NH_4OH for the removal of COS. The fourth impinger contains a KOH/alcohol solution for the selective removal of CS_2.

This sampling system is inexpensive to assemble and use and provides an accurate measure of COS in effluents which are relatively clean. If the source to be sampled has a significant particulate level a filter should precede the first impinger to avoid plugging of the impinger frit.

The sampling for $(CN)_2$ is based on the ability of aqueous base to hydrolyze cyanogen to cyanide (CN^-) and cyanate (OCN^-). For laboratory tests the $(CN)_2$ was passed through two impingers in series containing 0.1 M NaOH to determine the effeciency of $(CN)_2$ removal. The results show only a trace quantity of $(CN)_2$ in the second impinger suggesting adequate scrubbing of the gas stream using a single impinger. These experiments were conducted on an ideal gas stream and for field use at least two impingers in series should be used.

Adsorbent trap sampling techniques of COS and $(CN)_2$ were also evaluated as a part of this program. The procedures and trapping media tested have been previously discussed in Section 4.1. Although the adsorbent techniques met with some success the breakthrough volumes for COS and $(CN)_2$ were low enough that trace level determination in real effluent samples would not be possible. The best adsorbent trap studied proved to be the Porapak QS system previously described.

Analysis of Carbonyl Sulfide and Cyanogen --

The analysis of the impinger traps for carbonyl sulfide and carbon disulfide was accomplished by oxidation of the impinger solution using hydrogen peroxide (H_2O_2) to form sulfate ($SO_4^=$) from the entrained sample. A barium salt is added to the product solution and the sulfate determined as barium sulfate gravimetrically. The entire test can be conducted in the field or shipped to an off-site laboratory. The results of a field

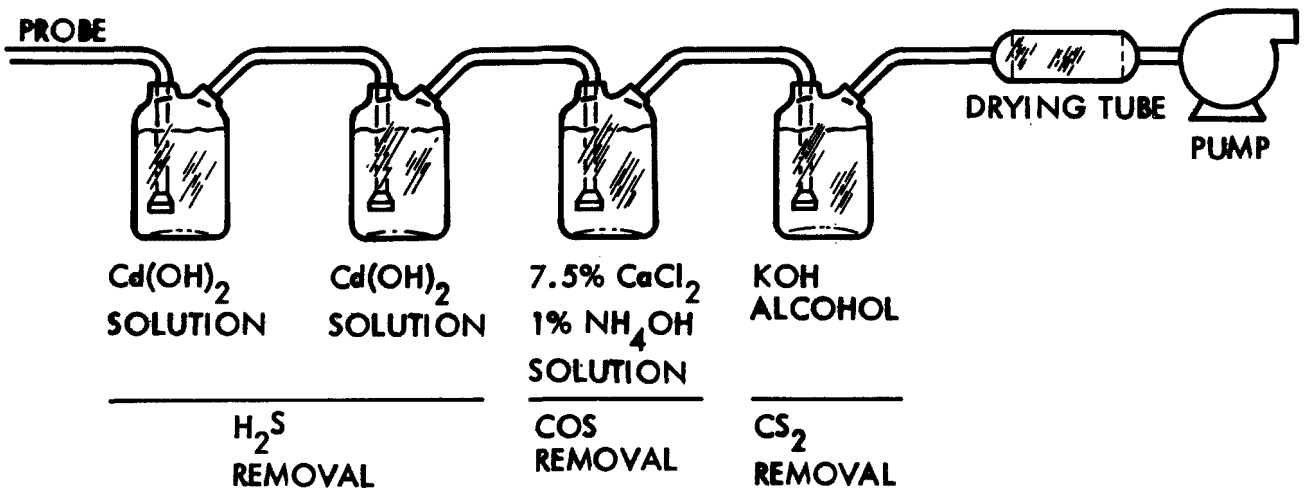


FIGURE 4-20 Impinger Sampling System for COS and CS_2

verification test of this procedure are given in Table 4-11. The results and observation of the test suggests that H_2S interference may still be a significant problem. Further work must be done to fully evaluate this procedure before it is routinely applied to all sources of COS.

The analysis of cyanogen collected using the basic impingers discussed above was accomplished by a modified Werner procedure. The modified Werner method for the determination of cyanate depends on the formation of a blue copper-pyridine-cyanate complex which is extracted from an aqueous solution with chloroform. The modified method is the result of selecting an optimum addition of pyridine and copper sulfate solution for the test. Color intensity is reduced by extreme conditions of pH, but a change of buffer pH from 5.0 to 8.0 caused only a 5% loss in sensitivity. A pH slightly above 6, using the cacodylate buffer, was selected since gradual decomposition of cyanate can occur at or below pH 5.5. Color stability is excellent over extended periods, if evaporation of chloroform is prevented.

The cyanate determination was performed directly in the 0.1 M NaOH impinger solution. The basic impinger solution may also contain $S^=$, CN^-, and RS^- ions, all of which are candidates for interferences in the OCN^- determination. These possible interferences may be delt with simply by determining the OCN^- after the evolution of the aforementioned species by acidification and helium purging. No field tests were conducted using this procedure and possible interferences have not been fully evaluated, however the acidification step prior to the cyanate determination should remove many of the potential interferences such as HCN and H_2S.

The analysis of adsorbent trapped samples is conducted as previously discussed in Section 4.1. The analysis by gas chromatography using selective detectors (i.e., thermionic (N/P) alkali flame for $(CN)_2$ and flame photometric for H_2S) provides for clean chromatograms and reproducable results. The errors which are associated with the adsorbent sampling techniques significantly over shadow the analytical finish. The ease of analysis associated with adsorption trapped samples leads one to hope for future developments in the area of selective adsorbents for specific reduced inorganic compounds. If this is accomplished full utilization of the recently developed highly specific and sensitive gas chromatographic detectors can realized.

Table 4-11

Field Verification Results of Samples Taken at The Paraho Oil Shale Demonstration Facility

Sample	Volume of Air Sampled (M^3)	Concentration COS (ppm)	Concentration CS_2 (ppm)
9/6-1	0.013	13	18
9/6-2	0.022	ND [1]	ND [1]
9/6-3	0.022	20	ND [1]

1 ND = Not Detected

Where approprate concentrations are suspected, grab sampling techniques can be employed. The techniques for both grab sampling and analysis have been discussed in detail (Section 4.1) and are applicable to $(CN)_2$ and COS when care is exercised.

SECTION 5.0

SUGGESTIONS FOR FURTHER RESEARCH

A description is provided in this report of the methodology for the sampling and analysis of representative reduced inorganic compounds from a variety of sources. Further research is required before the proposed methodology can be routinely used in the field. Some of the additional research required includes:

- Evaluate complex samples for interferences.
- Determination of the recovery of all reduced species in mixtures described by a statistical matrix.
- Determination of the storage life of samples collected, i.e., impinger and adsorbent trapped samples.
- Complete characterization of Porapak QS and other specialized materials for use in adsorbent traps for selective compound sampling.
- Design and evaluation of cartridge-type adsorbent traps that can be stored for extended periods before and after use without changes in efficiency for sampling or degradation of trapped samples.
- Establish conditions to permit rapid sampling and analysis of higher molecular weight amines and mercaptans.
- Choose from existing sources or design selective detectors for the identification and determination of reduced inorganic species.
- Improve or design new on-site monitors for reduced inorganic species in effluent streams.

The sampling and analysis of reduced inorganic species is a very

important area of study. Very few current environmental assessment programs are using compound specific techniques for sampling and analysis. Therefore little information is being gained on the true risk associated with a given source.

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16. ABSTRACT The report describes Level 2 sampling and analysis procedures for determining emission rates of specific reduced inorganic compounds, including metal and non-metal hydrides, sulfides, carbonyls, and elements. For the report, a reduced inorganic compound is a metal or non-metal that is bound to hydrogen (in its zero valence state) or to carbon. It includes a literature review identifying (1) industries where reduced inorganic compounds are likely to be found, and (2) sampling and analysis methods previously used to identify and quantitate inorganic compounds. The literature review identifies sampling methods that have been applied to reduced inorganic compounds and analysis techniques that can identify compound structure, rather than just total elemental emissions. The procedures given in the report are detailed and, for the most part, specific to individual compounds. Accuracy, interferences, and detection limits have been determined for manyof the species under laboratory conditions. Some of the procedures were tested as part of a field study at a shale oil conversion plant.

17. KEY WORDS AND DOCUMENT ANALYSIS

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