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Environmental Protection Technology Series

**FIELD TESTING:
TRACE ELEMENT AND
ORGANIC EMISSIONS FROM
INDUSTRIAL BOILERS**



**Industrial Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711**

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October 1976

FIELD TESTING:
TRACE ELEMENT AND ORGANIC EMISSIONS
FROM INDUSTRIAL BOILERS

by

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LIMITATIONS ON APPLICATION OF DATA REPORTED

The data cited in this report are trace element emissions. These emission levels are suitable for use in estimating mean emissions from industrial inventories. However, they are not suitable for predicting emissions from any one boiler or as regulatory limits or trace element emission standards.

ABSTRACT

Sampling of four coal fired industrial boilers was conducted to determine the emissions of 19 trace and minor elements and polycyclic organic matter (POM). The emissions of the trace and minor elements were related to total quantities of each element present in the fuel by examining the degree of mass balance and element partitioning based on fuel input and element output in furnace deposits, fly ash and flue gas vapor. The tendency of volatile elements for enrichment of finer particulate was examined by analysis of cascade impactor samples.

Measured output of elements classified as high in volatility, tended to be less than the fuel input, attributed to possible low collection efficiency of sampling equipment for vapor phase elements. These same elements were found to be more highly concentrated in the fly ash opposed to furnace deposits and to have higher concentrations in the smaller particle sizes. Elements classed as medium or low volatility tended to be more uniformly distributed with respect to both partitioning in the boilers and particle size. Mass output results for these elements frequently exceeded goal input indicating possible sample contamination by boiler or sampling system construction materials.

The presence of four specific POM compounds was indicated in the coal, ashes and stack gases but results were highly variable.

CONTENTS

<u>Section</u>	<u>Page</u>
ABSTRACT	iii
FIGURES	vii
TABLES	ix
ACKNOWLEDGEMENT	xi
1.0 INTRODUCTION	1
2.0 SUMMARY	3
2.1 Material Balance	7
2.2 Particulate Partitioning	9
2.3 Particulate Enrichment	11
2.4 Polycyclic Organic Material (POM)	11
2.5 Conclusions	15
3.0 BACKGROUND	17
3.1 Source of Trace Elements	18
3.2 Source of Polycyclic Organic Material	19
4.0 SAMPLE COLLECTION AND ANALYSIS	22
4.1 Sample Collection	24
4.2 Sample Analysis	32
4.3 Particulate Size	47
4.4 Material Balance	54
5.0 FIELD TEST, ORIGINAL COLLECTION TRAIN	59
6.0 FIELD TEST NO. 166, MODIFIED COLLECTION TRAIN	62
6.1 Boiler and Fuel Characteristics	66
6.2 Collection Train	71
6.3 Species Concentration	72

CONTENTS (Continued)

<u>Section</u>		<u>Page</u>
7.0	FIELD TEST NO. 169, MODIFIED COLLECTION TRAIN	79
7.1	Test Results	79
7.2	Boiler and Fuel Characteristics	83
7.3	Collection Train	86
7.4	Species Concentrations	88
8.0	SPECIAL REAGENT COMPARISON TEST	95
8.1	Sample Collection Equipment	95
8.2	Analytical Methods and Data	99
8.3	Results	100
9.0	ELEMENT PARTITIONING AND PARTICULATE ENRICHMENT	111
9.1	Element Partitioning	115
9.2	Particulate Size	121
9.3	Particulate Enrichment	132
10.0	REFERENCES	140
11.0	CONVERSION FACTORS	144

FIGURES

<u>Number</u>		<u>Page</u>
2-1	Field test site locations and location numbers	4
2-2	Material balance	8
2-3	Element partitioning of cobalt, iron and copper	10
2-4	Particulate enrichment of antimony and manganese	12
2-5	Polycyclic organic material (POM)	13
3-1	Trace element concentrations in coal	19
4-1	Trace element collection train schematic	23
4-2	Ice bath portion of collection train showing gas flow direction and bubbler identification numbers	25
4-3	Schematic diagram of Kapton liner inside probe tube	31
4-4	General procedure for sample treatment and analysis	36
4-5	Required analyses for trace element	42
4-6	Sample processing and analysis flow chart	43
4-7	Required analyses for cascade impactor catch	43
4-8	Detail of one stage and of precutter cyclone for cascade impactor	49
5-1	Reagent set recommended following initial tests	61
6-1	Material balance test run numbers 166-9, 166-10, and 166-11	63
6-2	Boiler schematic showing gas flow paths and sampling port location	69
7-1	Material balance, test run no. 169-3	80
7-2	Solid particulate emissions at baseload, coal fuel	87
8-1	Test boiler installation	97
8-2	Sampling train schematics	98
8-3	Material balances for the three sample collection trains	108
9-1	Partitioning of moderately volatile elements	116
9-2	Partitioning of moderately volatile elements	117

FIGURES (Continued)

<u>Number</u>		<u>Page</u>
9-3	Partitioning of highly volatile elements	118
9-4	Partitioning of highly volatile elements	119
9-5	Particulate size distribution, coal fuel and chain grate burner	126
9-6	Particulate size distribution, pulverized coal fuel	127
9-7	Baseline particulate size distribution, No. 6 oil fuel	129
9-8	Baseline particulate size distribution, No. 6 oil fuel	130
9-9	Particulate enrichment by moderately volatile elements	133
9-10	Particulate enrichment by moderately volatile elements	134
9-11	Particulate enrichment by highly volatile elements	135
9-12	Particulate enrichment by highly volatile elements	136

TABLES

<u>Number</u>		<u>Page</u>
3-1	Trace Element Concentrations in U.S. Crude Oil	20
3-2	Benzo[alpyrene Emissions From Coal- and Oil-Fired Boilers in the U.S.	21
4-1	Trace Species Distribution in Sampling Train	27
4-2	Sample Probe Lining Materials and Selection Criteria	28
4-3	Candidate Filter Material for Trace Specie Sampling	33
4-4	Approximate Elemental Contents of Several Filter Types	34
4-5	Feasibility of Analytical Methods	37
4-6	Analytical Sensitivity of Spectroscopy Techniques	38
4-7	Recommended Chemical Analysis Methods	41
4-8	Carcinogenic Polycyclic Organic Material	47
6-1	Chloride, Fluoride and Sulfate Material Balance	65
6-2	Organics Emissions	67
6-3	Boiler, Coal, and Ash Characteristics	70
6-4	Species Concentration	73
6-5	Species Concentration	75
6-6	Species Concentration	77
7-1	Chloride, Fluoride and Sulfate Emissions	82
7-2	Organics Emissions	82
7-3	Boiler, Coal and Ash Characteristics	85
7-4	Species Concentrations	89
7-5	Species Concentrations	91
7-6	Species Concentrations	93
8-1	Test Boiler and Fuel Data Summary	101
8-2	Trace Species Train Characteristics	102
8-3	Trace Element Content of Coal and Ashes	103
8-4	Trace Element Analysis of Train M	104
8-5	Trace Element Analysis of Train T	105
8-6	Trace Element Analysis of Train S	106

TABLES (Continued)

<u>Number</u>		<u>Page</u>
8-7	Material Balances by Three Calculation Methods	109
9-1	Particulate Size	123
9-2	Cascade Impactor Data Summary	131
9-3	Particulate Size and Enrichment	138
9-4	Particulate Size and Enrichment	139

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SECTION 1.0

INTRODUCTION

Concern for trace element emissions has received impetus from published reports of the widespread atmospheric dissemination of certain of these substances, especially mercury, as the result of fossil fuel use.^(1,2,3) The elements that commonly are considered to be among the most toxic are beryllium, fluorine, arsenic, selenium, cadmium, lead, and mercury.⁽⁴⁾ Under Part 61 - National Emission Standards for Hazardous Pollutants, Title 40 CFR, the U.S. Environmental Protection Agency has promulgated national emission standards for mercury, beryllium, and asbestos.⁽⁵⁾ Appropriate future research programs and control technology may be developed from field testing of trace element and organic emissions from industrial boilers.

Emissions from industrial boilers are of concern because fuel combustion in stationary sources accounts for 21% of the total criteria air pollutant emissions⁽⁶⁾ and a significant part of these emissions may be trace elements. The objective of the field test and analysis work was to determine the fly ash particle size distribution and to identify and quantify the gaseous and particulate trace species emissions from oil and coal-fired industrial boilers.

Trace species emission measurement was added to an existing two-year field test program to evaluate the application of combustion modifications to control the pollutant emissions from industrial boilers.^(7,8) Five boilers from the existing program were selected for tests, and the additional testing of these boilers for trace species emissions yielded data at minimum time and cost. While criteria pollutant emission testing took precedence over the trace specie emission testing, it did not significantly compromise the trace emission measurements. Results of criteria pollutant emission tests are given in Reference 8.

The specific trace elements and the compounds selected for identification and quantification are as follows:

Antimony, Sb	Cobalt, Co	Tellurium, Te
Arsenic, As	Copper, Cu	Tin, Sn
Barium, Ba	Iron, Fe	Titanium, Ti
Beryllium, Be	Lead, Pb	Vanadium, V
Cadmium, Cd	Manganese, Mn	Zinc, Zn
Calcium, Ca	Mercury, Hg	Chlorides
Chromium, Cr	Nickel, Ni	Fluorides
	Selenium, Se	Sulfates

The polycyclic organic material (POM) selected for identification and quantification are as follows:

- 7,12 Dimethylbenz[a]anthracene
- Benzo[a]pyrene
- 3 Methylcholanthrene
- Dibenz[a,h]anthracene
- Benzo[c]phenanthrene
- Dibenzo[a,h]pyrene
- Dibenzo[a,i]pyrene
- Dibenzo[c,g]carbazole

Quantification of the polychlorinated biphenyl (PCB) emissions was also attempted.

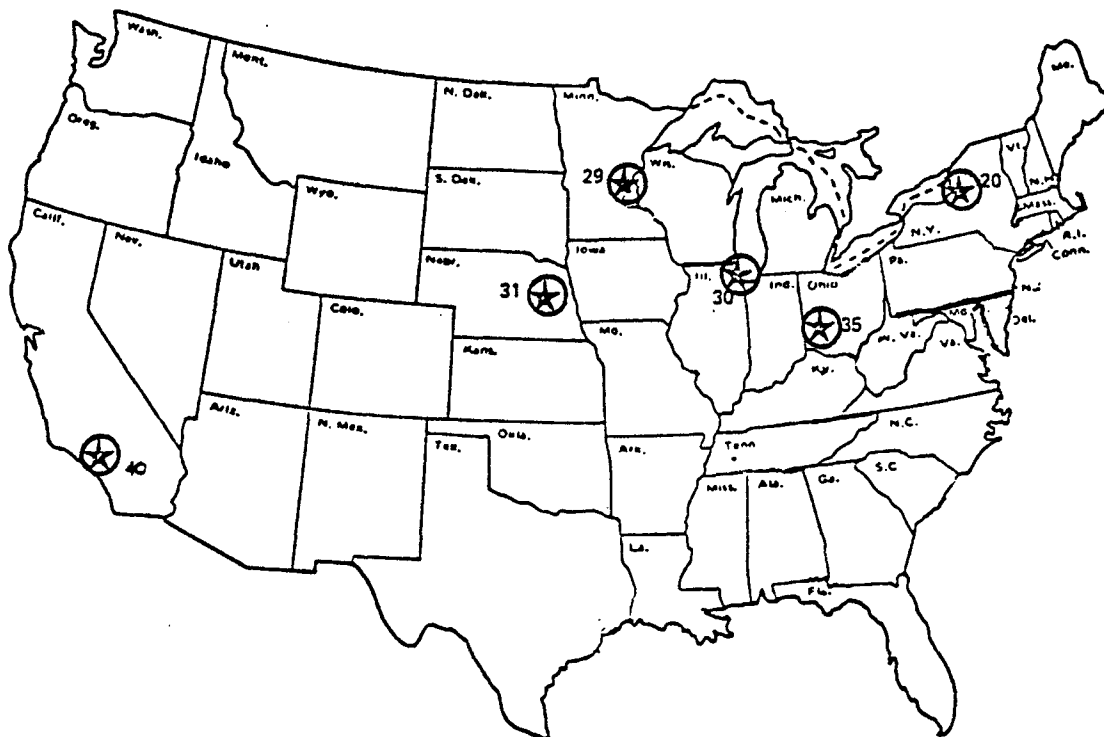
SECTION 2.0

SUMMARY

The objective of the field test and analysis work was to quantify the gaseous and particulate emissions of certain elements and organic compounds from oil and coal fired industrial boilers. The intent was to utilize existing trace species sampling concepts that had been developed for the Environmental Protection Agency by other contractors rather than to develop new ones. The data obtained were to be used to define the need and requirements for emission control technology development and for an appropriate research program.

The sampling method employed was a collection train consisting of a probe, cyclone and filter for particulates, and a liquid impinger train with eight bubblers. A trap for organics was placed between the third and fourth bubbler. This trap contained Tenax GC as the adsorbent.

The specie emission testing was done at the six locations shown by the circled stars in Figure 2-1. However, shortly after the field testing was started at the first test site, it was found that the concept upon which the design of the sample collection apparatus was based did not provide for adequate collection efficiency of volatile elements, such as mercury. Additional development of the collection procedure was needed. Consequently, the program evolved into two parts: (a) field test of chemicals used to scrub the species out of the flue gas to determine the best chemicals and collection method, and (b) field tests using the chemicals and collection method selected as a result of part (a). The final test of collection chemicals and methods was comprehensive and included a material balance of several of the species, as well as a comparison of the effectiveness of several chemicals.



- ⊙ Locations where trace element measurements were made.
(in order of test) are:
- 29 - St. Paul, Minnesota
 - 30 - Chicago, Illinois
 - 35 - Piqua, Ohio
 - 31 - Fremont, Nebraska
 - 20 - Rochester, New York (samples collected, not analyzed)
 - 40 - Santa Ana, California

Location numbers as assigned in a previous program ^(7,8)

Figure 2-1. Field test site locations and location numbers.

Topics of the sections that discuss test results are as follows:

<u>Report Section No.</u>	<u>Topic</u>	<u>Field Test Site Location Number</u>
5	Field evaluation of original collection chemicals and procedures	29,30
6	Field test of an early collection train design with crushed coal	35
7	Field test of an early collection train design with pulverized coal	31
8	Final evaluation of three trains (In lieu of Location 20 sample analysis)	40

The first trace species test was done at Location No. 29 with oil fuel. Except for the usual equipment "shakedown" troubles, no sample collection problems were encountered. However, when the contents of the first three bubblers were analyzed for mercury, very little was found. After study and discussion by those involved in the program, it was concluded that the distilled water that had been used in the first two bubblers was unsatisfactory as a mercury collector at isokinetic collection flow rates. The collected samples were analyzed no further.

The second trace species test was delayed pending a resolution of the mercury collection problem. It was later performed at Location 30 to compare the trace element collection efficiency of four different reagents.

After review of the analytical results for Locations 29 and 30, and independent results obtained by MRI, Inc. at other locations under a separate contract with the EPA, it was decided that KVB, Inc. should resume trace species sampling at Location 35. The boiler at this location was a coal-fired, chain-grate type. It was also decided that a reagent set developed for the EPA trace species program by TRW Systems, Inc., Redondo Beach, California, would be used to trap the mercury. It was expected that the latter reagent set could trap mercury at the higher pumping rate necessary for isokinetic sample collection.

When the "TRW reagent", ammonium hydroxide, was used at Location 35, the trace species train repeatedly plugged because the granular Tenax adsorbent

became hygroscopic and stopped the flow of flue gas. Previously, the Tenax adsorbent had not picked up water.

After a number of special test runs and consultations, it was concluded that the cause was the ammonium hydroxide reagents used to trap mercury. The flue gas at Location 35 had a high sulfur content. Apparently the sulfur in the flue gas reacted with the ammonium hydroxide in the first two bubblers and formed an ammonium/sulfur compound that caused the Tenax to become hygroscopic. As the Tenax became wet, it was no longer granular and the flue gas could not be pumped through it. The ammonium hydroxide was replaced by a sodium carbonate-based reagent in the first two bubblers to neutralize the sulfur compounds. With the sodium carbonate reagent, the trace species tests were run with no further problems.

The KVB field crew then went to Location 31 to test the pulverized coal fired boiler there for trace species. No collection train problems were encountered at Location 31.

The next trace species test was done at Location 20 in conjunction with combustion modification testing. There were no difficulties. However, the EPA Project Officer directed that the samples collected not be analyzed because the analysis of the samples from Locations 31 and 35 indicated that mercury collection still was not completely satisfactory. Also the analytical laboratory reported that the probe liner that now was part of the train design was high in organics and possibly could cause the organic analysis to be in error. The funds saved by cancelling the analysis were to be used for a sixth test.

After discussion with those concerned with trace species collection train design, the EPA Trace Element Project Officer decided to cancel the trace species test on oil fuel scheduled at Location 19. Instead, a test was planned where the three existing toxic species train configurations could be operated side-by-side and their collection efficiencies compared. This comparison test was done using the small coal fired boiler located in the KVB, Inc. laboratory in Santa Ana, California, Location 40.

Investigation of collection chemicals and methods resulted in rejecting the original concepts as unsatisfactory and perceiving the need for new concepts. The original design of the collection train ultimately proved to be unsatisfactory for collection of a sample of the volatile elements from the flue gas when the train was operated at isokinetic flow rates. Development of a new collection train, designated Source Assessment Sampling System (SASS) train, has been undertaken by the U.S. Environmental Protection Agency and will be evaluated for future trace species sampling work, rather than the configurations that are discussed here.

The degree of success of the collection train designs was determined by investigating three emission phenomena, (1) material balance, (2) species partitioning and (3) particulate enrichment.

2.1 MATERIAL BALANCE

The degree of material balance for each of the elements of interest was evaluated using information from the field tests, and the results are shown in Figure 2-2. Mass balances were judged to be acceptable when the total quantity of an element present in the collected ashes and stack gas was within 75 to 125% of the amount present in the fuel. The basis for this criteria is discussed in Section 4.1.1.

Most elements that are not expected to volatilize during combustion tended to be balanced or overbalanced. Barium, iron, manganese and titanium were overbalanced in some tests. Calcium balanced well in three of four tests. Cobalt was underbalanced in all tests.

Elements that are expected to volatilize during combustion tended to be underbalanced, particularly arsenic, selenium, cadmium, zinc, lead and tin. However, copper and the most volatile element, mercury, were within the acceptable balance range for two and three of the four measurements, respectively.

Elements with volatility characteristics that are not clearly defined tended to be balanced or overbalanced. These elements include chromium, nickel, and vanadium.

ELEMENT COLLECTED / ELEMENT IN COAL, %

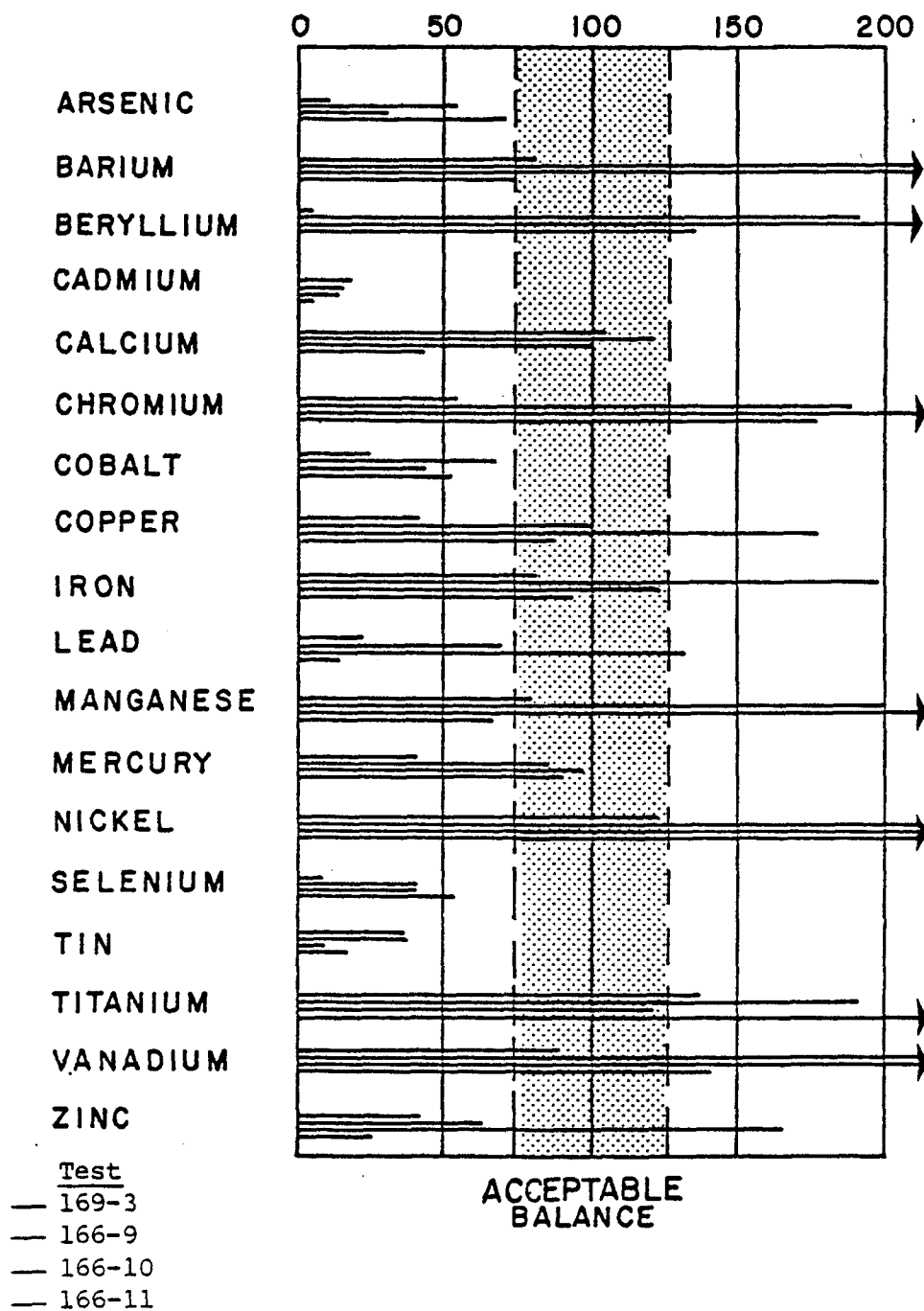


Figure 2-2. Material balance.

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The unacceptable balances, particularly of the more volatile elements were attributed to low collection efficiency of the bubbler liquids for these elements. A significant portion of the elements that entered the boiler with the coal evidently were vaporized and passed through the filters and bubblers without being condensed. In future tests, the degree of balance could be improved by using scrubber chemicals that have a higher collection efficiency than those used in the three trains and by reducing the velocity of the flue gas through the bubblers. Isokinetic flow rates were used for the tests in order to get a particulate catch that was truly representative of the actual trace element particulate distribution in the flue gas.

2.2 PARTICULATE PARTITIONING

Element partitioning theory predicts that certain elements will tend to be concentrated in certain parts of the boiler, depending upon the temperature of the flue gas in that part. Highly volatile elements will tend to be deposited in increasing concentrations on the fly ash as the flue gas carrying it cools in passing through the boiler. The less volatile elements will tend to condense early or not vaporize at all, and remain in a more uniform concentration throughout the boiler. Results of the field tests were in accordance with partitioning theory.

The partitioning of low-volatility iron, moderately volatile cobalt, and highly volatile copper is illustrated in Figure 2-3. Concentration in terms of micrograms of cobalt per gram of particulate upstream of the dust collector increased over the cobalt concentration in the coal and then remained relatively constant in the collector and downstream of the collector. There was little partitioning between the bottom ash, the fly ash upstream of the collector and the fly ash downstream of the collector. Iron condensed in the furnace and then maintained a relatively constant concentration in the fly ash as it moved to the cooler downstream parts of the boiler.

The tendency of the highly volatile elements to deposit on the fly ash as the flue gas cools is illustrated by the distribution of copper shown in Figure 2-3. Copper concentration on the fly ash increased steadily as the flue gas moved to successively cooler parts of the boiler.

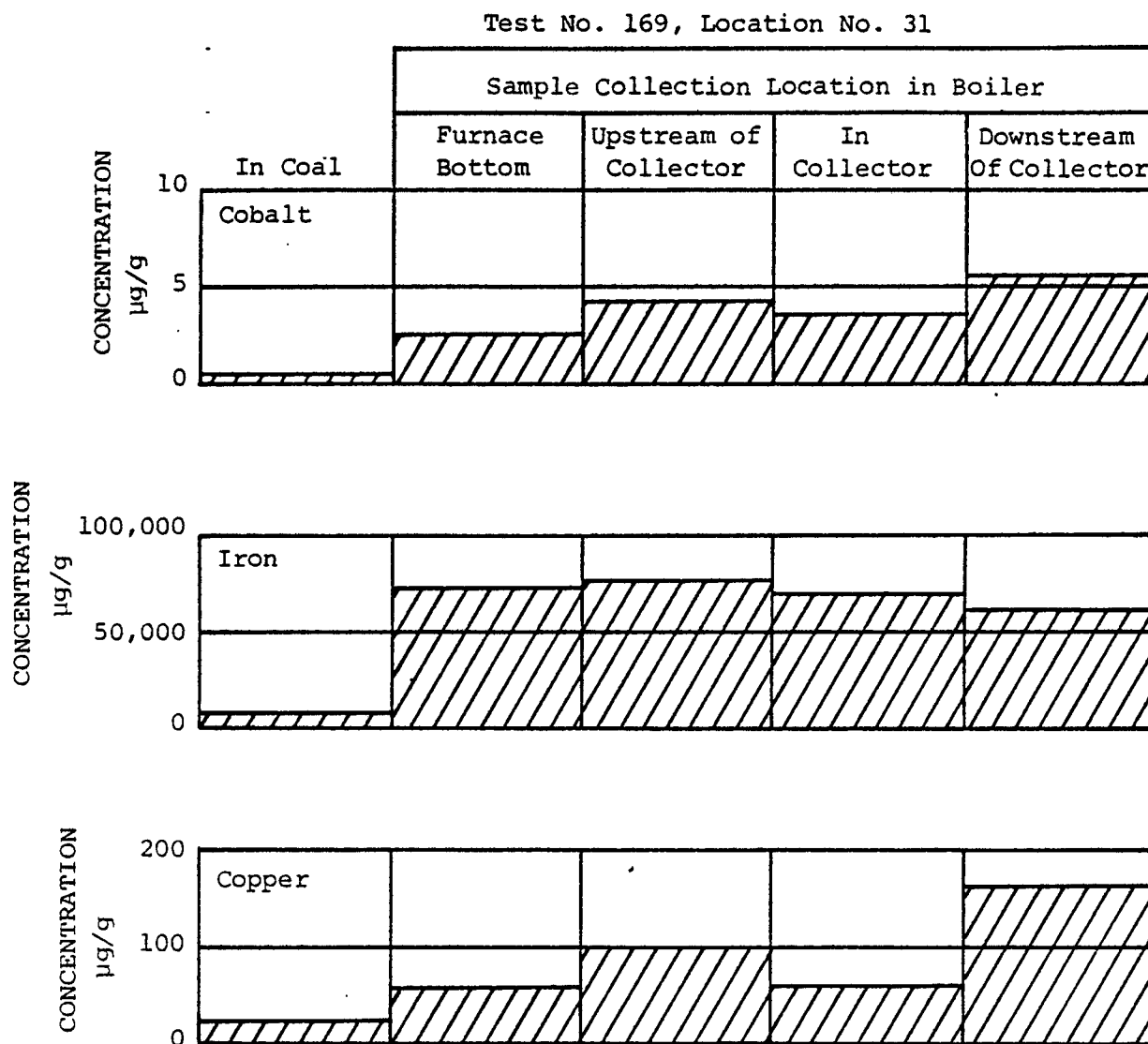


Figure 2-3. Element partitioning of cobalt, iron, and copper by location in the boiler.

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2.3 PARTICULATE ENRICHMENT

A third aspect of trace element emissions that was studied was particulate enrichment. Particulate enrichment theory predicts that those elements that are volatile at the 1800 K temperature of combustion tend to condense or absorb on the smaller size fly ash. Because the finer fly ash particles have a higher surface area per unit mass than do the coarse particles, they will contain a relatively higher concentration of the more highly volatile elements. Those elements that are less volatile in the combustion zone condense to form the fly ash upon which the volatiles later condense.

Particulate size results from the field tests were consistent with particulate enrichment theory, as illustrated in Figure 2-4 by the increase in the concentration of antimony at the particulate size decreased. Results for the less volatile manganese, on the other hand, did not exhibit a well-defined increase in concentration as the particulates became smaller. A detailed discussion of the results of particulate enrichment investigation is presented in Section 9.0.

2.4 POLYCYCLIC ORGANIC MATERIAL (POM)

The measured emissions of polycyclic organic material (POM) for six runs during two tests are summarized in Figure 2-5. An open circle indicates an analysis that found no POM, and a shaded circle an analysis where POM was found. For example, POM No. 2, benzo[a]pyrene, was found in the coal of Test 166 but not in the coal of Test 169. Test 169 has two rows of circles under ashes; the top row indicates when POM was found in the bottom ash and the lower row when it was found in the dust collector ash. There is only one row of circles for Test 166 because the bottom and collector ashes were combined within the boiler and there was only one ash sample for each of the three runs.

The concentrations of the individual POM's are tabulated in Sections 6 and 7. It was found during analysis that the amount of flue gas fly ash that was collected was inadequate for a quantitative analysis. Therefore, the discussion that follows is limited only to the POM's that were present in the bottom and collector ashes and in the bubbler liquid.

Test No. 169, Location No. 31

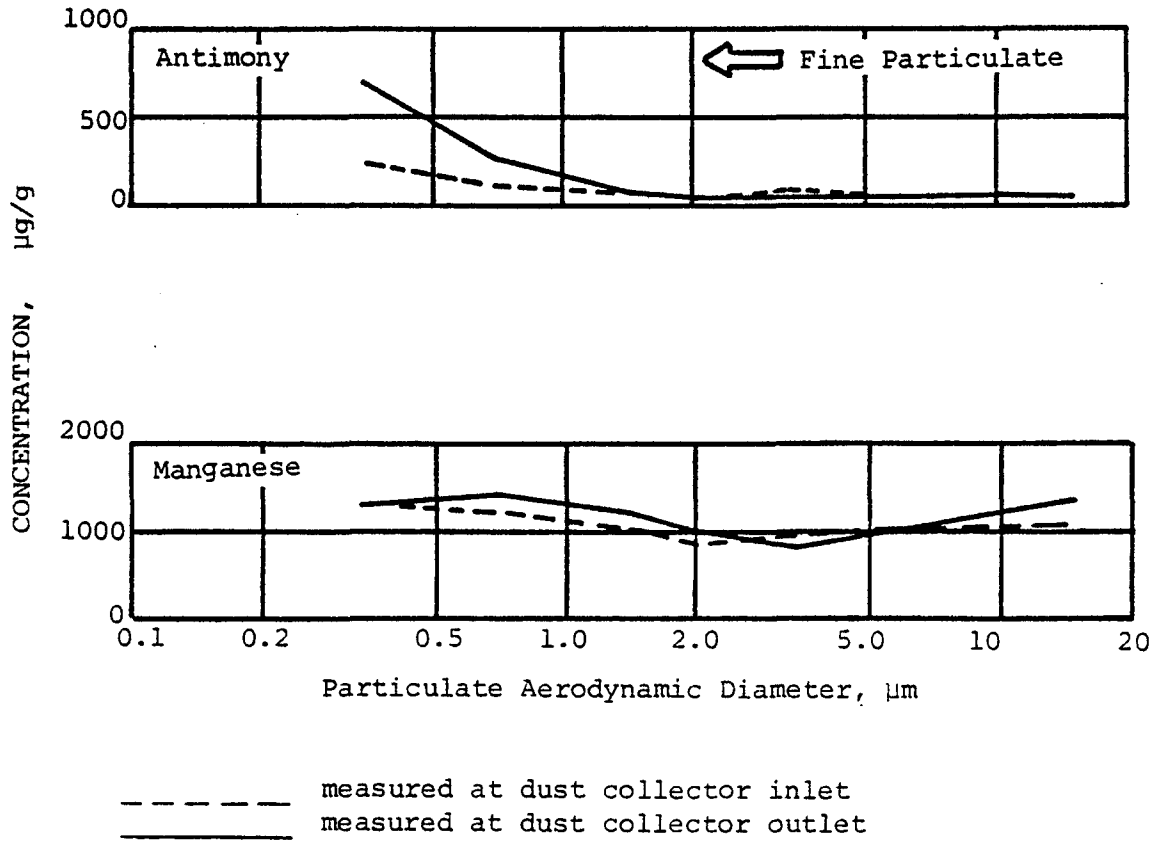


Figure 2-4. Particulate enrichment of antimony and manganese.

Test No.		Location Where Found								
		Coal			Ashes			Stack Gas		
POM-1	166	○	○	○	○	●	●	○	●	○
*7-12										
dimethylbenz	169	○	○	○	○	○	○	○	○	○
[a]anthracene					○	○	○			
POM-2	166	●	●	●	●	●	●	○	○	○
*benzo[a]										
pyrene	169	○	○	○	●	●	○	●	●	○
					●	○	●			
POM-3	166	○	○	○	○	○	○	○	○	○
3 methyl-										
cholanthrene	169	●	●	●	○	●	●	●	●	M
					●	●	●			
POM-4	166	●	●	●	○	○	○	○	○	○
*dibenz[a,h]										
anthracene	169	●	○	●	○	○	○	○	○	M
					○	●	○			

○ : Analysis found no POM

○ : Analysis found some POM

M : Data missing

*Instruments calibrated for isomer shown. The presence of these isomers relative to other isomers was not verified.

Figure 2-5. Polycyclic organic material (POM).

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POM No. 1 (7 - 12 dimethylbenz[a]anthracene) was found in the combined bottom and collector ashes of two of the runs of Test 166. The quantity was 2.2 grams or less, which was less than the emissions of the other POM's by a factor of ten or more. It also was found as a vapor in the stack gas downstream of the collector in one run. This POM was not found at all in Test 169.

POM No. 2 (benzo[a]pyrene) was present in the coal of Test 166 and also in the ashes. It was not present as a vapor in the stack gas. In Test 169 it appeared in four of the six ash samples and in two of the three stack gas samples. The concentration decreased at the successive downstream locations in the boiler which indicates that it was not being partitioned, as were the elements.

POM No. 3 (3-methylcholanthrene) was not encountered at all during Test 166, but it was present throughout the boiler in Test 169. The concentration was successively less at the downstream point in the boiler.

POM 4 (dibenz[a,h]anthracene) appeared in the coal of both tests, but it appeared in only one ash sample downstream.

With regard to POM 1, 2 and 4, the analytical instruments were calibrated for the specific isomers indicated. However, it was not possible to distinguish isomers by the methods used. Therefore, while POM-2 was assigned as the isomer benzo[a]pyrene, isomers other than the [a] isomer could have been present in part or in total, and similarly for isomers of the other POM compounds.

It was not possible to identify four desired POM by the methods used. These four were benzo[c]phenanthrene, dibenzo[a,b]pyrene, dibenzo[a,i]pyrene, and dibenzo[c,g]carbazole.

2.5 CONCLUSIONS

1. Sample collection methods based on modifications of EPA Method 5 sample trains proved to be unsatisfactory for collection of volatile metals based on mass balance criteria. This was attributed to low collection efficiencies of the liquid bubblers in the sampling train. Reduction of sample flows, increased bubbler size or different collection chemicals, should be investigated as means for improved collection efficiency while maintaining isokinetic sampling flow rate.

2. Material balances for trace elements varied from less than 10% to over 200% recovery of the amount of element input in the fuel. Elements that were most difficult to recover included antimony, arsenic, cadmium, cobalt, lead, selenium, tin and zinc. An excess amount was recovered most frequently for barium, beryllium, chromium, manganese, nickel, titanium, and vanadium. Acceptable recovery was achieved most frequently for calcium, copper, and iron. While recovery of mercury was judged acceptable in several tests, the majority of the mercury was found to be contained in boiler ashes rather than in flue gas vapor. This is contrary to results of other studies and to the volatile nature of mercury.

3. The results for partitioning of the elements at specific points in the boilers were consistent with expected partitioning characteristics. The more volatile elements were deposited in increasing concentrations on the ash as the combustion gases passed to successively cooler parts of the boiler system. The less volatile elements were more uniformly distributed.

4. The results for particle size enrichment were also in agreement with expected enrichment characteristics. The more volatile elements tended to concentrate on the smaller size particles, while the less volatile elements were more uniformly distributed with particle size.

5. Polycyclic Organic Matter (POM) was found to be present in some of the coal, ash and stack gas vapor samples. Samples were analyzed for four specific POM compounds. All four compounds were found to be present but not in all samples. The quantity of stack gas particulate samples collected was not sufficient for determination of POM. The data for presence and quantity of each POM compound in different parts of the boiler and for replicate samples were not sufficiently consistent to allow positive conclusions regarding the formation or emissions of these compounds.

SECTION 3.0

BACKGROUND

Current studies of the trace species air pollutant problem indicate that fossil fuel combustion in stationary sources such as industrial boilers may be a major source of these pollutants on a national level.^(9,10) The burning of coal and oil in industrial boilers is of concern because these fossil fuels contain a variety of potentially toxic trace elements, such as mercury, which may be discharged into the atmosphere in significant concentrations. In addition, the incomplete combustion of coal and oil produces carcinogenic polycyclic organic compounds.⁽¹¹⁾

The environmental impact of potentially toxic trace species pollutants generated by fossil fuel combustion in industrial boilers may be much greater than the emissions themselves would suggest, because some pollutants are emitted in the form of vapors or fine particulates which are not collected by conventional pollutant control devices. The small size of trace pollutants may intensify any adverse health effects because particulates of this size penetrate the natural filters of the human respiratory tract and they may not be expelled. Moreover, these fine particulates are enriched in trace element content above what is found in natural aerosols.

Primarily on the basis of volatility profiles, fossil fuel burning is expected to introduce measurable quantities of arsenic, mercury, cadmium, tin, antimony, lead and zinc to the atmosphere. A study designed to detect fallout from a major coal burner equipped with a precipitator showed that cadmium, cobalt, chromium, iron, mercury, nickel, titanium and zinc were deposited in the soil over a 3000 square kilometer area, and with the exception of mercury, the soil deposit correlated with the respective metal concentrations in the coal.⁽¹²⁾

Mercury, being more volatile, was more widely disseminated. Previous work had indicated that mercury exists primarily as a vapor in the flue gas and consequently as much as 90% of it bypasses any electrostatic precipitation control device. (13,14) Other work in the field shows evidence that selenium and arsenic may follow a similar pattern. (15,16,17,18)

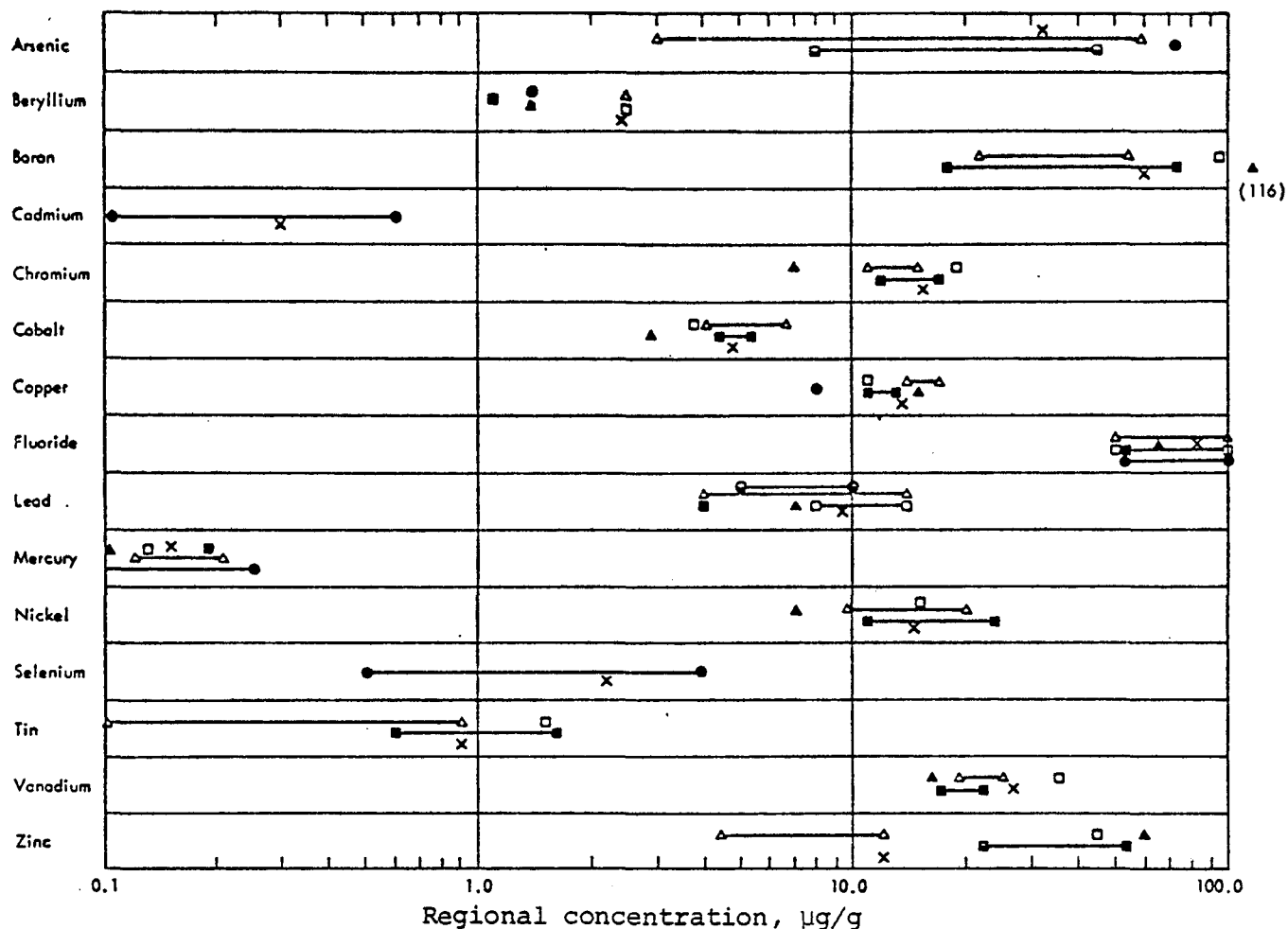
In an analysis of airborne coal fly ash, it was found that ten elements, (lead, antimony, cadmium, selenium, zinc, arsenic, nickel, chromium, beryllium, and manganese) were concentrated in the smaller size particles. (19) Mercury, although not studied, was expected to follow suit because of its high volatility. Another study of lead and cadmium reported similar findings. (20) Atmospheric vanadium, as well as selenium, antimony, and zinc, arising principally from residual fuel combustion, showed a pattern similar to coal emissions. (10,21,22) The magnitude of fine particulate emissions, their low collection efficiency, their low deposition rates, and their ease of dissemination in the free atmosphere may increase the health risk of receptors.

3.1 SOURCE OF TRACE ELEMENTS

An analysis of the origin of coal and oil fuels found that: (1) nearly all of the coal consumed by power plants comes from two coal mining regions of the country: the Appalachian (56%) and Interior Eastern (34%) regions; and (2) most of the domestic crude oil originates from three states--Texas, Louisiana, and California. Of the total amount of crude oil processed in the United States, approximately 85% is produced domestically while the balance is imported. Of the domestic production, 11% is produced in California, 25% in Louisiana, 34% in Texas and 30% elsewhere. (22,23)

The information available on the trace and minor elements in coal and oil was analyzed to determine representative concentrations in the fuel from each producing region. The results for coal are shown in Figure 3-1. (23) The figure gives the extremes in average concentration of trace elements for over 90% of the beds within each coal producing region. Other investigators have reported iron concentrations in coals ranging from 100 $\mu\text{g/g}$ to 30,000 $\mu\text{g/g}$ and titanium concentrations ranging from 100 $\mu\text{g/g}$ to 1,000 $\mu\text{g/g}$. (10) Mercury concentrations from 0.012 to 33 $\mu\text{g/g}$, with an average value of about 0.2 $\mu\text{g/g}$

Element



LEGEND

Symbol	Region	States Included
△	Appalachian (A)	Pennsylvania, Ohio, West Virginia, Maryland, Virginia, Eastern Kentucky, Tennessee, Alabama (and Georgia)
□	Interior-Eastern (IE)	Illinois, Indiana, Western Kentucky, Michigan
■	Interior-Western (IW)	Iowa, Missouri, Nebraska, Kansas, Oklahoma, Arkansas, Texas
○	Western (W)	Wyoming, Idaho, Utah, Colorado, New Mexico, Arizona, Washington
●	Southwestern (SW)	Utah, Colorado, Arizona, New Mexico
▲	Northern Great Plains (N)	Montana, North Dakota, South Dakota
x	Weighted Average	

Figure 3-1. Trace element concentrations in coal. (23)

6001-48

have been found in certain U.S. coals. (13,22,24,25,26) The concentrations of most trace and minor elements vary considerably from seam to seam with a coal bed, and the variations within a bed frequently are greater than the differences between the averages for different beds.

The trace element content of crude oil by region is listed in Table 3-1. (27)

3.2 SOURCE OF POLYCYCLIC ORGANIC MATERIAL

Polycyclic organic material (POM) is formed in the combustion of coal, oil, and natural gas fuels, or, more generally, of any compound that contains carbon and hydrogen. The amount of POM formed will vary widely since highly efficient combustion favors very low POM emissions and inefficient burning favors high emissions. Thus, combustion modifications that reduce the nitrogen oxides emissions may increase the emissions of POM.

Although the mechanism of POM formation in combustion processes is complex and variable, a relatively clear picture of the overall reaction has emerged. Chemical reactions in flames proceed by free-radical paths, and radical species containing one, two, or many carbon atoms can combine in rapid fashion at the high temperature attained in the flame front. This pyrosynthesis of pyrolysis products is a function of many combustion variables, and

TABLE 3-1. TRACE ELEMENT CONCENTRATIONS IN U.S. CRUDE OIL (27)

Element	Concentration, $\mu\text{g/g}$			Weighted Average
	Origin of Crude			
	California	Louisiana	Texas	
Antimony	<0.007	0.05	<0.01	<0.024
Arsenic	<0.007	0.05	<0.12	<0.08
Barium	<0.06	0.09	<0.14	<0.11
Manganese	0.018	0.027	<0.05	<0.04
Nickel	77	4.4	3.3	16
Tin	<0.6	0.5	<1.0	<0.8
Vanadium	48	1	1.9	9.0

one of the most important is the presence of a chemically reducing atmosphere which is common in the center of flames. In a reducing atmosphere, radical chain propagation is enhanced, allowing the buildup of a complex POM molecule, such as benzo[a]pyrene. Although methane can lead to POM, the formation of these large molecules is favored by the presence of higher molecular-weight radicals and molecules in fuels such as oil and coal as opposed to natural gas⁽¹¹⁾.

Polycyclic organic material is emitted from a vast number of stationary sources and some urban areas close to significant POM sources are subjected to high atmospheric POM concentrations. Inefficient combustion of coal in hand-fired residential furnaces produces large amounts of benzo[a]pyrene as shown in Table 3-2.⁽²⁸⁾

TABLE 3-2. BENZO[A]PYRENE EMISSIONS FROM COAL-
AND OIL-FIRED BOILERS IN THE U.S. (28)

Type of Unit	Gross Heat Output, Joules/hr	Benzo[a]- pyrene Emission, kg/year
Coal		
Hand-stoker residential furnaces	0.10×10^9	381 000
Intermediate units (chain- grate and spreader stokers)	$63-263 \times 10^9$	9 000
Coal-fired steam power plants	$1.05-2.11 \times 10^{12}$	900
Oil		
Low-pressure air-atomized	0.7×10^9	1 800
Other	$0.02-22 \times 10^9$	1 800

6001-48

The low benzo[a]pyrene emission found in power plants, burning crushed or pulverized coal, relative to the emissions from the less-efficient hand-stoked furnaces implies that, for a given fuel, the efficiency with which combustion takes place is the controlling factor in benzo[a]pyrene emissions.

SECTION 4.0

SAMPLE COLLECTION AND ANALYSIS

The U.S. Environmental Protection Agency is developing methods to collect and analyze certain metals, gases and organics that are present in the exhaust gases from boilers. Trace species testing was added to the Phase II of the industrial boiler program because it was convenient and cost effective.

A survey of the current trace species measurement and analysis methods resulted in selection of the method developed by Midwest Research Institute, Kansas City, Missouri (MRI).

The MRI sample collection concept consisted of a gaseous sample collection "train" made up of a flue gas collection probe, cyclone and filter in a heated oven and an ice bath that contained eight bubblers and a solid filter in series. (29)

In addition to particulate and vapor collection with the train, a sample of the fly ash was collected with a five-stage cascade impactor to determine the size distribution of the fly ash and the enrichment distribution by trace species for a given particulate size. For coal fuel tests, a cyclone was added to the inlet end of the impactor to collect the larger size particulate.

The trace species collection concept of MRI is shown schematically in Figure 4-1. The sample collection and the gas flow measurement sections (delineated in Figure 4-1) were standard EPA Method 5 items. All of the sample collection hardware performed satisfactorily. However, problems were encountered with the chemicals that were used in the bubblers to scrub out the metals and organics.

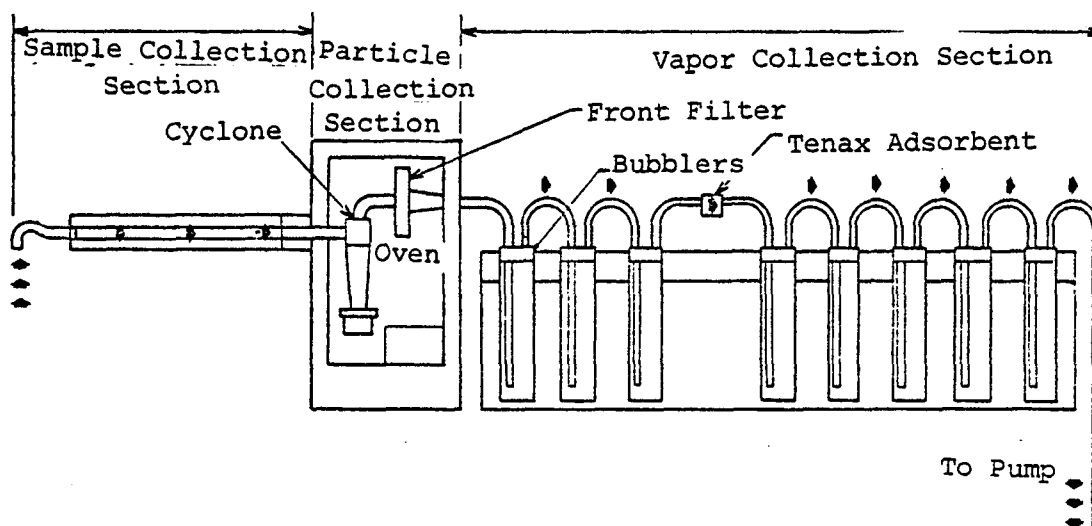


Figure 4-1. Trace species collection train schematic.

6001-48

4.1 SAMPLE COLLECTION

4.1.1 Particulate and Vapor

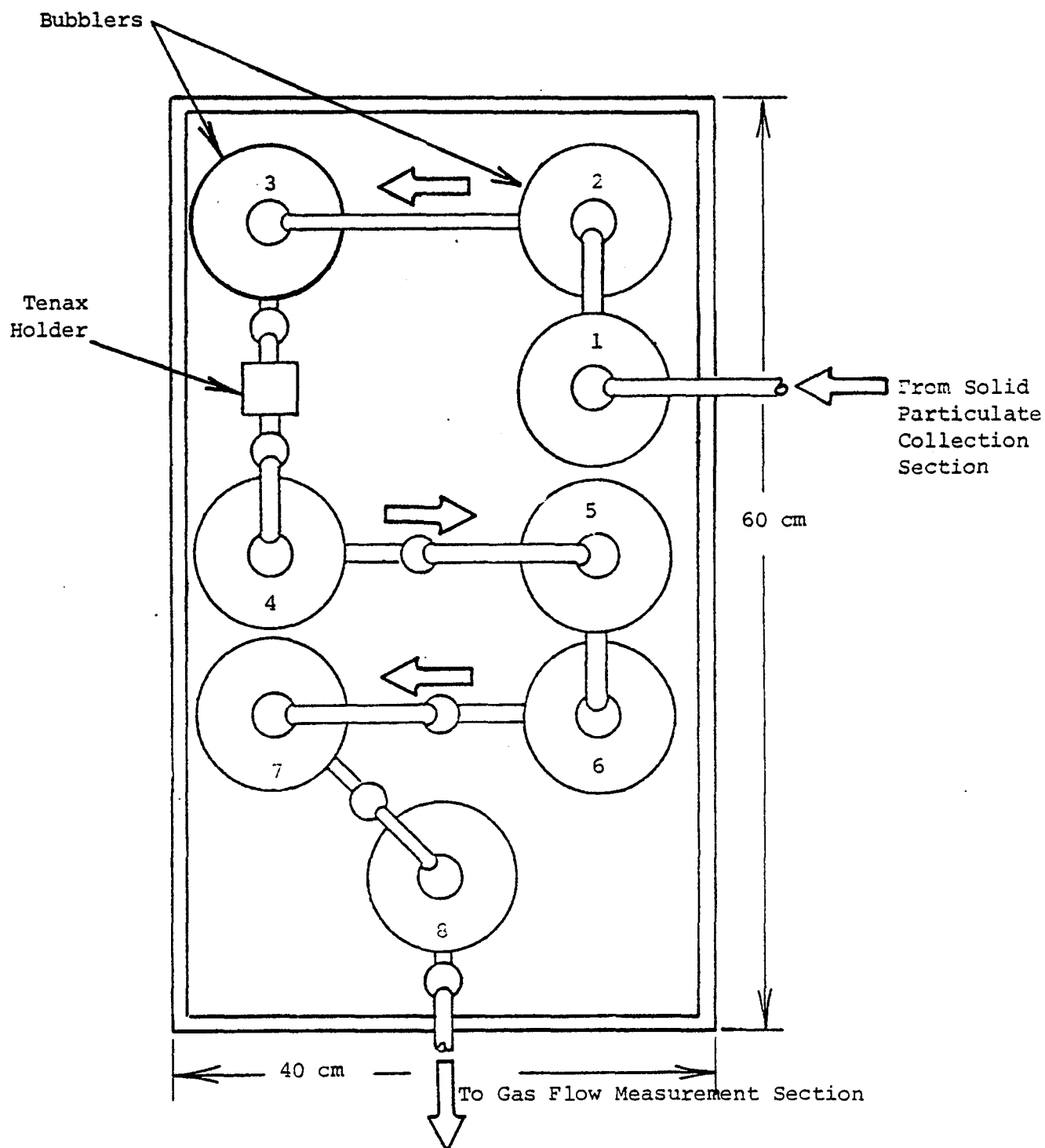
The solid particulate and gaseous sample collection and gas flow measurement sections of the collection train used were from an Emission Parameter Analyzer Model T1050 manufactured by the Joy Manufacturing Company for use in a standard EPA Method 5 particulate concentration measurement. The impinger box was replaced by a separate chilled water bath large enough to accommodate eight, rather than four, bubblers. A glass bulb was added between the third and fourth bubbler in which Tenax, a gas chromatograph column packing material, was placed to act as an organic adsorbent.

It had been found during prior testing that the temperature of the water bath must be maintained near 270 K (32°F) so that the stack gas would be cooled to less than 300 K (60°F) by the time it reached the Tenax adsorbent.⁽²⁹⁾ It is necessary to collect the organic sample at less than 300 K to obtain acceptable adsorption efficiencies. A mechanical refrigerator unit that was capable of reducing the temperature of the water in the ice bath chest to less than 275 K (41°F) was used.

Figure 4-2 is a schematic drawing of the top of the ice bath and shows the physical arrangement of the bubblers and the flue gas flow within the train. Bubblers were used in place of impingers in order to minimize flow resistance.

Sufficient material must be collected so that the sample can be analyzed accurately and precisely. Based on a need for determining source stream concentrations in the neighborhood of $60 \mu\text{g m}^{-3}$ (2.6×10^{-5} grains ft^{-3}) the sample collection rate was maintained near 0.0196 to $0.028 \text{ m}^3 \text{ min}^{-1}$ (0.7 to $1.0 \text{ ft}^3 \text{ min}^{-1}$) to collect $100 \mu\text{g}$ of the species of interest. Collection time depended upon the flow rate necessary for isokinetic sampling and was from 60 to 90 minutes.

Those species which existed as solid particulates at stack temperatures were collected in the glass cyclone or on the filter located in the heated oven. The volatile or submicron size species which behaved as gases were scrubbed out by the liquids in the bubblers. Different pollutants were collected by different sections of the train, depending upon the fuel composition,



Numerals on bubbler is the numeric designation of the individual bubbler.

Figure 4-2. Ice bath portion of collection train showing gas flow direction and bubbler identification numbers.

and an estimate of where the metals and gases were expected to be collected in the train is given in Table 4-1.⁽²⁹⁾ Table 4-1 indicates that 90% or more of the mercury and other volatile elements would be collected in the oxidation bubbler portion of the vapor train.

POM's were expected to be concentrated in the first three bubblers and in the Tenax adsorber. Most of the identifiable carcinogenic POM's, in tests to date, have been recovered with the solid particulates.⁽²⁹⁾ The Tenax adsorber was located in the train to extract all of the remaining POM's from the sample stream before it passed on to the bubblers that contained the oxidant.

A test normally consisted of three runs under identical boiler settings. A statistical analysis performed by MRI indicated that for three test runs a mass balance within $\pm 25\%$ tolerance for non-volatile elements could be achieved at a 90 percent confidence level. The mass balance tolerance was based on estimates of the expected input/output stream flow and concentration standard deviations.⁽²⁹⁾

4.1.2 Probe Material Selection

Standard stack sampling probes are heated tubes equipped with an outer protective sheath and a proper size nozzle for isokinetic sample collection. Materials of construction are typically 316 stainless steel, glass or quartz. Teflon often is used as a lining material. However, a Kapton liner may also be used. The relative merits of these materials as probe materials have been reported and are listed in Table 4-2.⁽³⁰⁻³¹⁾ Aluminum probes have the lowest operating temperature limit while quartz has the largest temperature range. Above approximately 523 K (480°F) aluminum and many of its alloys rapidly lose their physical strength; however, their light weight makes them attractive for particulate sampling in large diameter stacks.

Both glass and quartz are chemically inert except for the possible interaction of fluorine in the form of hydrogen fluoride, and neither would contribute to the contamination of trace element sampling. For sampling source streams that require a probe more than two meters long, however, glass and quartz become impractical because of breakage by vibration. Carbon steel,

TABLE 4-1. TRACE SPECIES DISTRIBUTION IN SAMPLING TRAIN⁽²⁹⁾

Species	Solid Particulate Collection Section		Vapor Collection Section	
	Nozzle and Probe	Cyclone and Filter	Moisture Condensing Impinger	Oxidative Impingers
Group A Al, B, Be, Ca Cr, Cu, Fe, Mn Mo, Ni, Si, Ag Sn, Ti, Zn	<10%	70%	20%	<5%
Group B As, Sb, Se	5%	45%	45%	5%
Group C Cl, F, Pb	<5%	20%	60%	10%
Group D Cd, Hg	<5%	<5%	<5%	>90%

6001-48

TABLE 4-2. SAMPLE PROBE LINING MATERIALS AND SELECTION CRITERIA (30,31)

Probe Material or Liner	Operating Temperature, K (°F)		Cleaning	Handling	Contamination/ Sample Alteration
Aluminum	523	(480)	Difficult	Light weight	Depends on alloy
Carbon steel	>1173	(1650)	Difficult	Heavy	Yes, possible Mn and other elements
Stainless steel (316)	1173	(1650)	Difficult	Heavy	Cr, Ni, other stainless elements
Titanium	>1273	(1830)	Unknown	Light	Depends on alloy
Glass (Borosilicate)	1093	(1500)	Difficult	Fragile	No contamination, possible loss of F
Quartz	>1773	(2730)	Difficult	Fragile	No contamination, possible loss of F
Kapton liner	723-773	(840-930)	Very easy	Satisfactory	None*
Teflon liner	<543	(520)	Easy	Satisfactory	None

*Although the references indicate no contamination with Kapton, Kapton may result in organic contamination.

while having a high temperature limit, is readily corroded by many stack gases and is a source of manganese and other elements. It has not been widely used for stack sampling. Teflon coated probes are excellent for trace element sampling from a contamination standpoint, but the maximum operating temperature of 543 K is too low.

Stainless steel is the probe construction material that was favored by KVB for field use. It has a high operating temperature limit and is readily available commercially. However, particulate material collected using stainless steel probe may contain nickel, chromium, and other alloy metals.

During sampling, particulate material is deposited on the walls as the flue gas is drawn through the probe, and the amount of material deposited on the probe walls could be significant, approaching a sizable proportion of the particulate material ultimately collected. This material must be washed from the probe and added to the material washed from the probe nozzle for the complete determination of emissions. Probe cleaning is difficult and time consuming under field test conditions. Rinsing and brushing are inadequate for strongly adhering particulates, leading to biased particulate loading results. For trace species sampling, the problems are compounded since the probe cleaning procedure exposes the collected sample and washings to contamination from the test site surroundings.

The sample collection probe used was a standard EPA Method 5 316 stainless steel design with a plastic liner developed by TRW Systems, Inc.,^(30,31) added. The plastic probe liner not only prevented contamination of the sample, but it also greatly facilitated sample collection and probe cleaning. The liner material used was a high-temperature, thermally-stable polyimide, called Kapton, which was manufactured by DuPont. Kapton is thermally stable in air to about 750 K (900°F) and has demonstrated ability up to 670 K (750°F) in flue gas streams. At present, there is no known organic solvent for the material, and it is infusible as well as flame resistant. Strong alkali, however, will dissolve Kapton. The results of a spark source mass spectroscopic analysis of the film material indicate that Kapton does not represent a significant source of contamination for trace element sampling, although there is some doubt about its suitability for organic material sampling.

Kapton was available as a sheet film 0.05 mm thick. A strip of material the length of the probe and 7.5 cm wide was cut from a roll of the film. The 7.5 cm width was enough to provide a double wall thickness when the liner was rolled inside the probe.

After cutting, the film strip was dried overnight in a desiccator. The strip then was tare-weighted and its weight recorded. Prior to a test the rolled film strip was inserted into a sampling probe, and the retainer bushing and sampling nozzle were added. The retainer bushing conducted stack gases and particulate past the end of the film preventing the stack gas from getting between the film and the probe wall. Figure 4-3 is a schematic of the Kapton liner and bushing inside the sample collection probe.

Upon completion of sampling the probe was disconnected from the solid particulate collection section and the nozzle was removed. With the end capped, the probe was taken back into the mobile laboratory and the liner was removed with a pair of forceps and placed inside a desiccator in a clean, labeled breaker to await reweighing.

As with the probe, possible sample contamination or alteration problems arise with the cyclone and filter. With stainless steel cyclones, the possibility of stainless steel alloying elements contaminating the samples may be greater than contamination from the probe because of the increased possibility of surface abrasion. A standard EPA Method 5 glass cyclone was employed whenever possible to reduce contamination problems.

The sampling train bubblers and connecting plumbing were another source of sample contamination, but this contamination was minimized by using well-washed glass containers.

4.1.3 Filter Selection

Filter materials that have been used for general particulate sampling contain small amounts of the very trace species being sought in the trace species testing. Extraction procedures developed

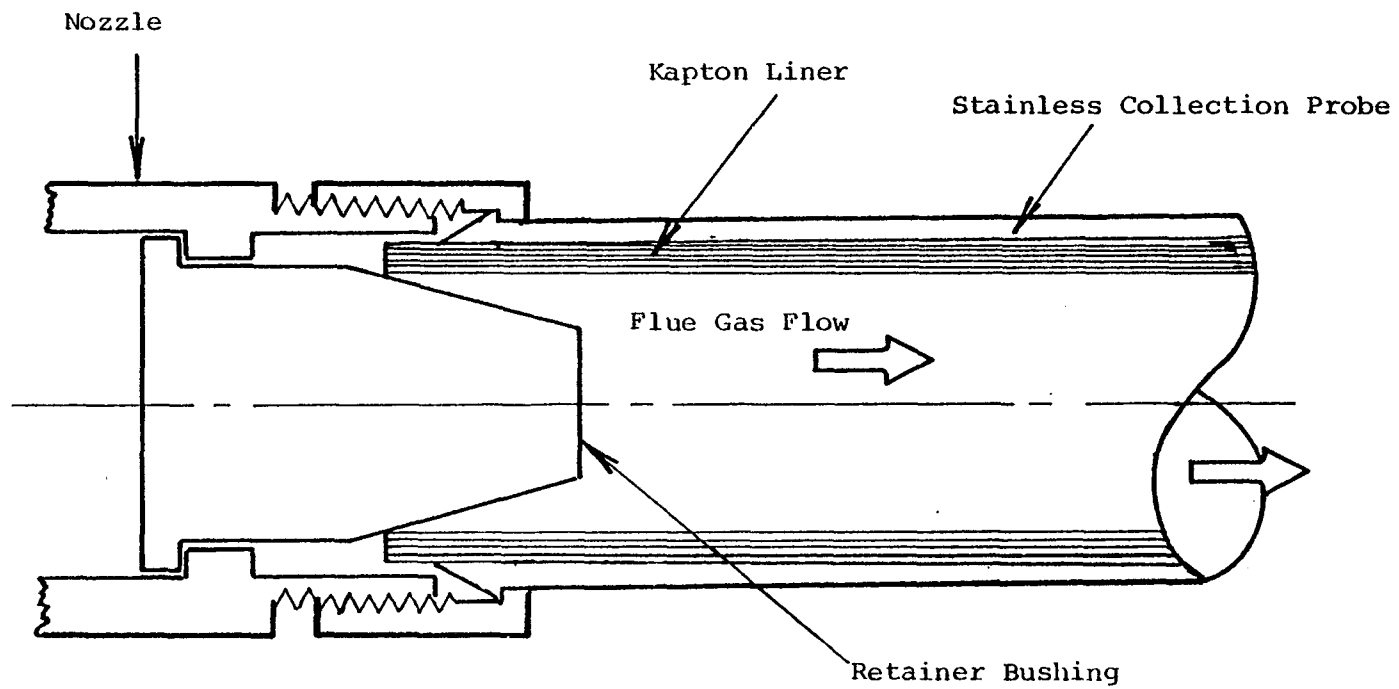


Figure 4-3. Schematic of Kapton liner inside probe tube. (30)

6001-48

by different laboratories for removing these contaminants have been only partially successful, and only recently have a few filter materials suitable for trace element sampling been developed.

Table 4-3 lists some of the filter materials, along with their relevant properties, that were considered for trace species sampling.⁽³⁰⁾ Of the materials in this table, two were tested in the field: Gelman Spectro Quality Type E with a siliconized surface and Tissuquartz. Typical trace species contents of both of these materials are listed in Table 4-4 and both were deemed to be acceptable.⁽³²⁾

However, it was found during sample analysis that when Gelman Type E filters were used as the final stage of the cascade impactor, the trace species background was so high relative to the concentration of the species deposited on it that the filter catch could not be analyzed. When the Tissuquartz material was tried in the field it was abandoned because it was too brittle for field use.

4.1.4 Sample Processing

All glassware used to store and/or transport components of the sampling train was cleaned by washing with detergent, rinsing with tap water, soaking in warm nitric acid, rinsing with distilled water, and rinsing with reagent grade acetone.

Subsequent to each run, the filters were removed from holders and placed in wide-mouth Wheaton glass bottles for shipment to the analysis laboratory. The probe tip, probe, and cyclone were rinsed with acetone and the rinses combined in a (Wheaton) glass bottle with a Teflon-lined screw cap. Absorbing solutions from the bubblers also were transferred into separate screw-cap Wheaton glass bottles and the bubblers were rinsed with acetone.

4.2 SAMPLE ANALYSIS

The pollutants that were sought consist of two major groups: polycyclic organic materials and elemental inorganic compounds. The latter group can be subdivided into those elements which form anions

TABLE 4-3. CANDIDATE FILTER MATERIAL FOR TRACE SPECIES SAMPLING (30)

Filter Material	Purity	Temperature Limit K (°F)	Filtering Efficiency	Ease of Handling ΔP	Strength
Carbon fiber (Kreha Corp.)	Good except for F	>770 (930)	Low	Low	Good
Cellulose paper (Whatman 41)	Poor	<470 (390)	Medium	Medium	Good
Graphite (Poco)	Excellent	>1300 (1800)	High	High	Good
Glass fiber, spectroquality (Gelman Instr. Co.)	Excellent	>270 (210)	High	Medium	Good
Microquartz fiber (Under development) (Arthur D. Little Co.)	Excellent	1000 (1830)	High	Medium	Good
Teflon membrane	Excellent	<1000 (480)	High	Extremely High	Good
Tissuequartz (Pollflex Co.)	Excellent	1000 (1470)	High	Medium	Poor
Sintered Silver	Excellent	<1200 (1650)	Undetermined	Medium	Good but corrodes readily

TABLE 4-4. APPROXIMATE ELEMENTAL CONTENTS OF SEVERAL FILTER TYPES⁽³²⁾

Element	Filter Type				
	Millipore AAWP (cellulose ester) mg/cm ²	Flotronics FM47-.8 (silver) mg/cm ²	Pallflex Tissuquartz mg/cm ²	Gelman (glass fiber) mg/cm ²	MSA (glass fiber) mg/cm ²
Be	<0.0003	<0.0003	<0.03	<0.03	<0.03
B	0.002	0.02	0.75	70.	60.
F	0.0003	0.1	--	--	--
S	0.006	0.2	0.03	2.	2.
Cl	0.0006	3.	1.	0.3	1.
Ti	2.	0.2	0.3	2.	0.1
V	0.0001	0.003	<0.05	<0.05	<0.05
Cr	0.002	0.06	<0.05	0.05	0.1
Mn	0.01	0.03	<0.05	0.3	<0.1
Co	0.00002	0.007	<0.05	<0.05	<0.05
Ni	0.001	0.1	<0.05	<0.05	<0.05
Cu	0.006	0.02	0.3	<0.05	<0.05
Zn	0.01	0.01	<0.5	40.	<0.5
As	--	<0.007	<0.5	<0.6	<0.5
Se	--	<0.007	--	--	--
Pb	--	<0.07	--	--	--
Cd	--	<0.03	<0.1	<0.1	<0.1
Sn	0.001	<0.01	<0.1	<0.1	<0.1
Sb	0.0001	<0.01	<0.1	<0.1	<0.1

(chlorides and fluorides) and those which form cations upon sample dissolution. Figure 4-4 depicts the general procedure used to divide the sample into these three groups.⁽²⁹⁾ Organic compounds were removed from the sample by extraction with benzene. Compounds of special interest, e.g., the highly carcinogenic benzo-[a]pyrene, is highly soluble in benzene; whereas elemental pollutants are insoluble in benzene except when present as organometallic complexes, which have limited solubility in benzene. The loss of inorganic pollutants was determined by elemental analysis of a number of benzene extracts, and it was not found to be significant. The benzene insoluble material was divided and analyzed for cationic and anionic pollutants.

Elemental analysis: A number of methods have been applied to the analysis of cationic elements. These include:

1. Atomic absorption (AA)
2. Inductively coupled plasma emission spectroscopy (ICP)
3. Neutron activation analysis (NAA)
4. X-ray fluorescence spectrometry (XFS)
5. Spark source mass spectrometry (SSMS)
6. Optical emission spectrometry (OES)
7. Electrochemical methods (EC--voltametry and potentiometry)

The feasibility of analyzing the collected samples for each of the elemental pollutants of interest by the methods mentioned in the preceding paragraph is indicated in Table 4-5. A plus indicates the analysis is feasible, a minus indicates the analysis is not feasible, and a circled plus indicates the analysis can be performed in the Midwest Research Institute laboratory. The criteria used to determine the feasibility of each analysis were the detection limits, sample requirements, and accuracy and precision of the method.

Detection limits: The detection limit of the method for coal and fly ash matrices was considered in the light of the expected concentration of the specie. If the detection limit was above the expected concentration, the method was indicated as not feasible. The detection limits of several spectroscopic techniques are shown in Table 4-6.⁽²⁹⁾

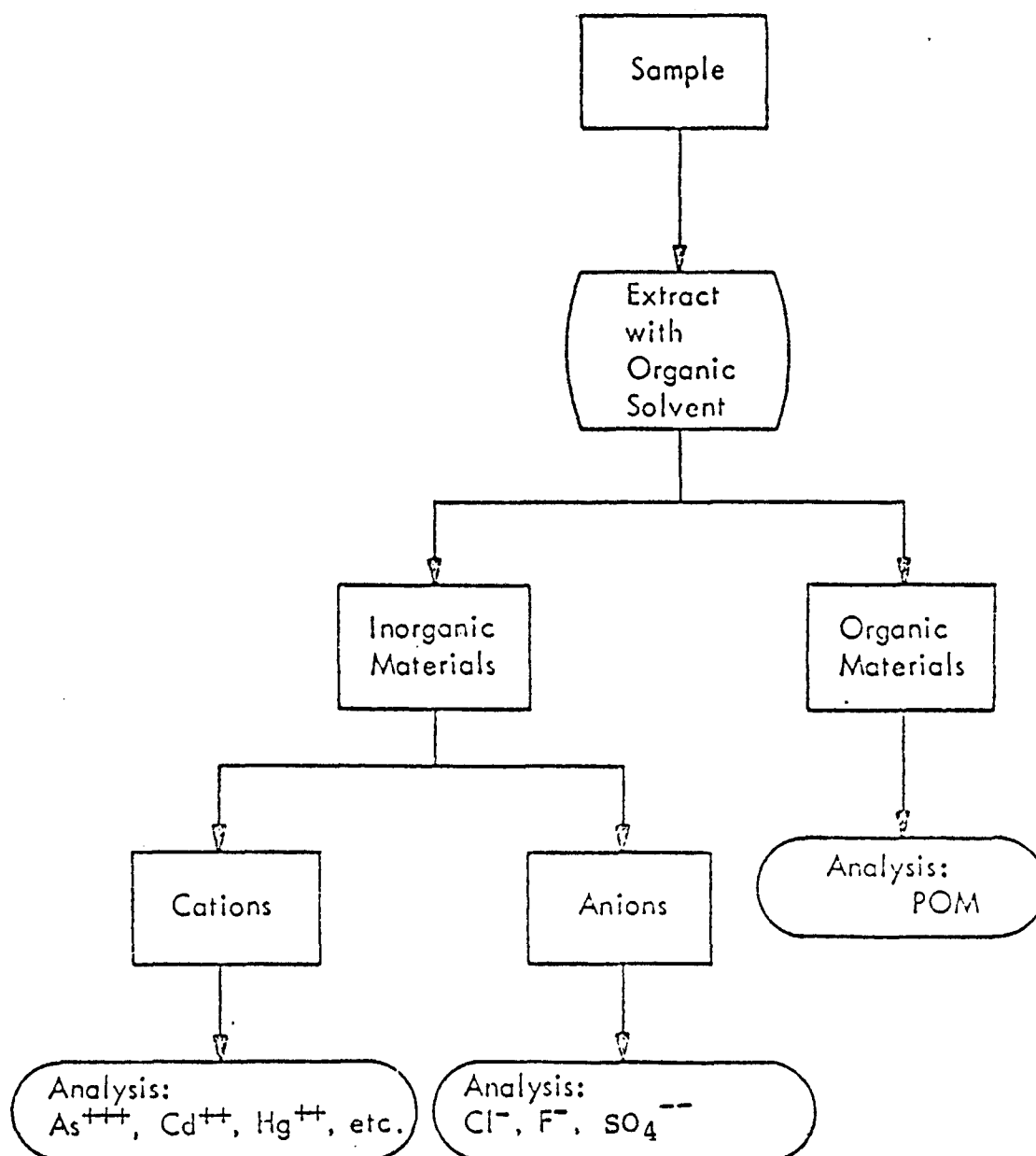


Figure 4-4. General procedure for sample treatment and analysis.

6001-48

TABLE 4-5. FEASIBILITY OF ANALYTICAL METHODS^{a/}

Elemental Pollutant	AA	AA, (micro)	ICP	NAA ^{b/}	XFS	OES ^{c/}	EC ^{d/}
Antimony	⊕ ^{e/}	-	-	⊕	-	⊕	⊕
Arsenic	⊕ ^{e/}	-	⊕	⊕	-	⊕	⊕
Barium	⊕	-	⊕	⊕	⊕	⊕	-
Beryllium	⊕	⊕	⊕	-	-	⊕	-
Cadmium	-	⊕	⊕	⊕	-	-	⊕
Calcium	⊕	⊕	⊕	-	-	⊕	-
Chromium	⊕	⊕	⊕	⊕	-	⊕	⊕
Cobalt	⊕	⊕	⊕	⊕	-	⊕	⊕
Copper	⊕	⊕	⊕	⊕	-	⊕	⊕
Iron	⊕	⊕	⊕	⊕	-	⊕	⊕
Lead	⊕	⊕	⊕	-	-	⊕	⊕
Manganese	⊕	⊕	⊕	⊕	⊕	⊕	⊕
Mercury	⊕ ^{f/}	-	-	⊕	-	⊕	-
Nickel	⊕	⊕	⊕	⊕	⊕	⊕	⊕
Selenium	⊕ ^{e/}	-	⊕	⊕	-	-	-
Tellurium	⊕	-	⊕	⊕	-	⊕	-
Tin	-	⊕	-	⊕	-	⊕	-
Titanium	⊕	⊕	⊕	⊕	⊕	⊕	-
Vanadium	-	⊕	⊕	⊕	⊕	⊕	-
Zinc	⊕	⊕	⊕	⊕	-	⊕	⊕
Chlorine	-	-	-	⊕	⊕	-	⊕
Fluorine	-	-	-	⊕	-	-	⊕

a/ The analytical procedures are as follows: AA, atomic absorption spectrophotometry; AA (micro), AA with carbon rod or other flameless atomization; ICP inductively coupled plasma; NAA, neutron activation analysis; XFS, x-ray fluorescence spectrometry; OES, optical emission spectrometry; EC, electrochemical methods.

b/ NAA methods include chemical pretreatment.

c/ OES methods include chemical pretreatment, photometric detection, DC arc (inert atmosphere).

d/ EC methods are anodic stripping voltametry and potentiometry (specific ion electrode for fluoride).

e/ Includes SbH₃, AsH₃, and SeH₃ generation and N₂-H₂-air flame.

f/ Cold vapor.

TABLE 4-6. ANALYTICAL SENSITIVITY OF SPECTROSCOPY TECHNIQUES ⁽²⁹⁾

Trace Element (cation)	Detection Limits *			
	CP Method (ng/ml)	Conventional Flame Methods (ng/ml)	Flameless Methods (ng/ml)	Hydride Methods (ng/ml)
Antimony	200	600.	20	4
Arsenic	40	1300.	20	4
Barium	0.1	300.		
Beryllium	0.5	20.	0.18	
Cadmium	2	20.	0.02	
Calcium	0.07	500.	10.	
Chromium	1	98.	1.0	
Cobalt	3	90.	1.2	
Copper	1	40.	1.4	
Iron	5	600.	20.	
Lead	8	160.	1.0	
Manganese	0.7	50.	0.1	
Mercury	200.	2000.	20.	
Nickel	6.	70.	2.0	
Selenium	30.	600.	20.	
Tellurium	80	300.	20.	
Tin	300	2000.	12.	
Titanium	3	2200.	-	
Vanadium	6	1200.	20.	
Zinc	2	12.	0.02	

* The concentration of a solution which produces a signal twice that of the background.

Sample requirements: If a method required a prohibitively large sample size (>1.0 g of particulate) or large dilution factors for multispecies analysis, it was indicated as not feasible.

Accuracy and precision: The accuracy and precision of the method must be sufficient to obtain an acceptable material balance for the specie in question. A relative standard deviation of $\pm 20\%$ was selected arbitrarily. Each of the methods indicated as acceptable meet this requirement in the most extreme situation (i.e., near a signal level of twice the noise level). At normal working levels, the feasible methods generally are within a relative standard deviation of 5%. Spark Source Mass Spectrometry (SSMS) is not listed in Table 4-5 because it did not meet these criteria. The NAA ratings are for methods which include chemical pretreatment. The Atomic Absorbtion (AA) (micro), and Inductively Coupled Plasma (ICP) methods are for one general sample pretreatment which consists of dissolving the sample. The AA and AA (micro) methods consist of consecutive single species determinations. The ICP method consists of up to 20 simultaneous species determinations which result in a multispecies scan similar to SSMS, but ICP results are more quantitative than SSMS.

Cost considerations are not reflected in Table 4-5. Because several chemical treatment procedures are required for NAA and OES analysis for the twenty elements of interest, these methods are more costly than AA or ICP analysis. The cost for ICP analysis is the same as AA for sample preparation, but due to the increased speed of analysis the cost per element quantified is somewhat less. The sensitivity of ICP is better than Flame AA and comparable to Micro AA techniques. Accuracy and precision for ICP are intermediate to Flame AA and Micro AA procedures. The costs for electrochemical analysis are similar to those for AA where satisfactory methods exist.

Gas chromatography, liquid chromatography and UV-visible spectroscopy have been applied to the analysis of POM.^(33,34,35) Identification should be verified by mass spectrometry if sufficient concentrations are present. Verification is accomplished most conveniently by a mass spectrometer interfaced directly with a gas chromatograph.

The methods of choice for both organic and elemental pollutant species are described in detail in the following section.

4.2.1 Analytical Methods

The methods of analysis that were used for each of the species are indicated in Table 4-7. The configuration of the collection train is shown in Figures 4-1 through 4-3 and one of the sets of reagents that was used is shown in schematic form in Figure 4-5. Several different sets of reagents were used in the bubblers during the program because the reagents still were undergoing development during the program. The set used for most of the program will be used here for illustration, and the reader is referred to the individual tests for a discussion of the particular collection reagents actually employed. Figure 4-6 is a flow chart of the sample processing and analysis of the bubbler reagents, the cyclone and front filter, and the Tenax adsorbent.

A schematic of the components of the cascade impactor and the analysis methods used to investigate possible selective enrichment of certain size particulates is shown in Figure 4-7.

Elemental pollutants (cations): Inductively Coupled Plasma Emission Spectroscopy (ICP) and Atomic Absorption Spectrophotometry (AAS) were used for the elements of interest.

Some of the advantages of ICP are: the low limits of detection for most of the trace elements of interest, the large number of elements which can be analyzed, the simultaneous multi-element determinations, the rapid analysis of large numbers of samples, nearly the same precision and accuracy of atomic absorption, the use of ultra-trace levels on μl or μg samples and the greatly decreased interference from matrix constituents.

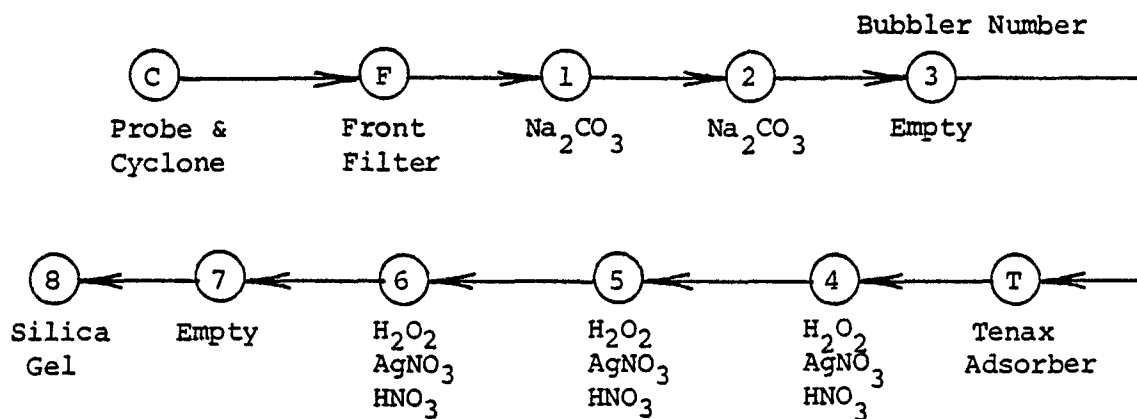
TABLE 4-7. RECOMMENDED CHEMICAL ANALYSIS METHODS ⁽²⁹⁾

<u>Pollutant</u>	<u>Method of</u>
<u>Trace Elements (Cations)</u>	<u>Analysis*</u>
Antimony	6
Arsenic	6
Barium	1
Beryllium	1
Cadmium	1
Chromium	1
Cobalt	1
Copper	1
Lead	1
Manganese	1
Mercury	7
Nickel	1
Selenium	6
Tellurium	2
Tin	2
Titanium	1
Vandium	1
Zinc	1
<u>Trace Elements (Anions)</u>	
Chlorine	3
Fluorine	4
Sulfate	8
<u>Organics</u>	
POM	5
<u>Minor Elements (Cations)</u>	
Calcium	1
Iron	1

*The methods of analysis are as follows:

- (1) Inductively Coupled Plasma Emission (ICP);
- (2) AAS, micro flameless methods;
- (3) AgNO₃ titration, electrochemical (EC) detection;
- (4) EC, Fluorine selective electrode;
- (5) Gas chromatography (GC), electron capture detection;
- (6) AAS, hydride generation method;
- (7) AAS, cold vapor method.
- (8) Barium perchlorate titration.

TRACE SPECIES COLLECTION TRAIN:



Collector Component Designation Analysis Method	C	F	1,2,3	T	4,5,6,7
Elemental	•	•			
POM	•	•	•	•	
Se, As, Sb, Hg	•	•	•		•
Particulates	•	•			

Figure 4-5. Required analyses for trace species collection train.

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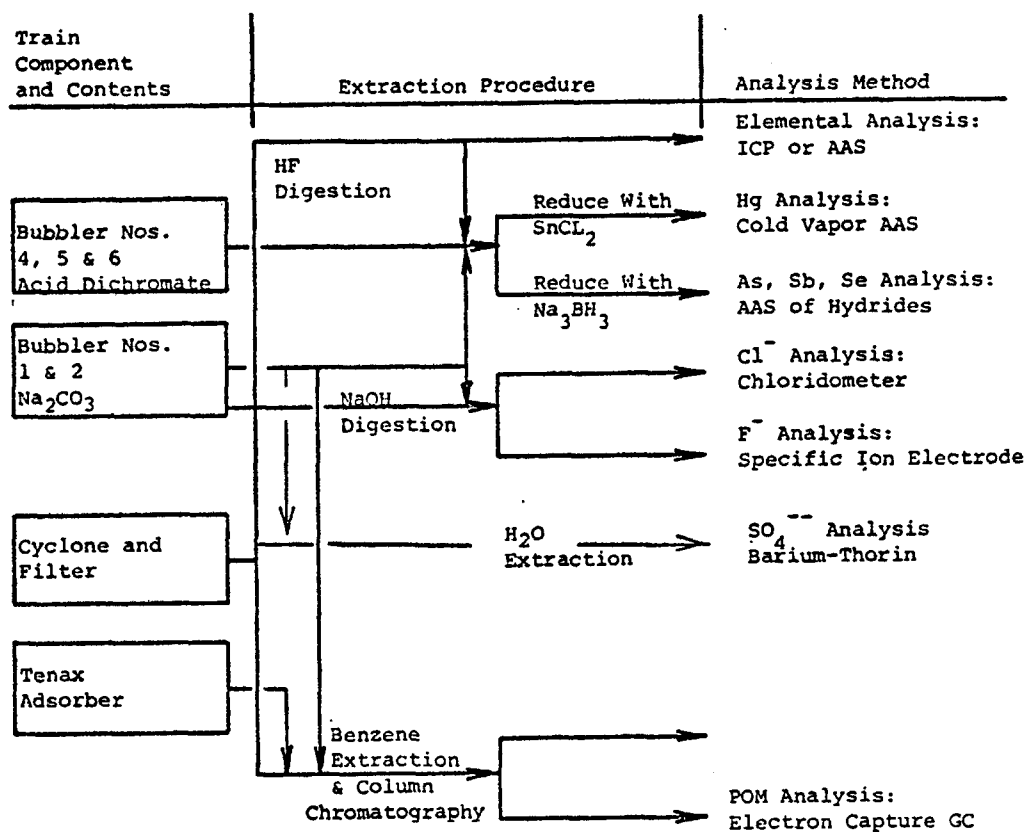
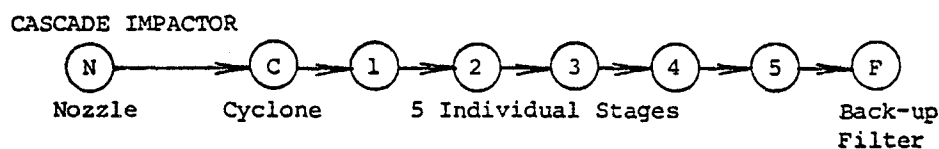


Figure 4-6. Sample processing and analysis flow chart.



Impactor Component Designation Analysis Method	Stage Nos. 1-5		
	N,C		F
A. Elemental	•	•	•
B. POM	•	•	•
C. Particulate	•	•	•

Figure 4-7. Required analyses for cascade impactor catch.

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Some of the advantages of AAS are: the low limits of detection for most of the trace elements of interest, the large number of elements which can be analyzed, the low cost of highly reliable instrumentation, and the accuracy and precision which can be obtained without highly trained technical personnel.

The combination of ICP and AAS gave added flexibility to the analysis procedures. Those elements which were of interest could be scanned by ICP, thus eliminating the cost of spark source mass spectroscopy. Most of the twenty elements of interest could be quantified by ICP techniques. For those elements which could not be determined by ICP, AAS was used. This combination of techniques allowed rapid analysis to meet the time requirements of the project. It also assured that a quality analysis was performed on all twenty elements of interest.

The recent development of the Inductively Coupled Plasma Emission method enables simultaneous analysis to be conducted on as little as 100 μ l of solution, hence reducing the total volume of solution required to analyze twenty elements from ≥ 25 ml to 1 to 5 ml. In addition, the solution detection limits are in the nanograms per milliliter range rather than micrograms per milliliter range required by conventional flame methods. In view of the analysis time required per sample, the number of samples involved with this project and the detection limits and accuracy required of the analytical methods, Inductively Coupled Plasma Emissions Spectrophotometry was chosen.

The sample preparation procedures for ICP and AAS depend upon sample matrices. For this investigation, the types of matrices were fuel, fly ash and bottom ash, sodium carbonate or ammonium hydroxide solution, and acid-dichromate or hydrogen peroxide solutions. A suitable preparation for these matrices is the acid-pressure decomposition technique developed by Bernas.⁽³⁶⁾ This technique

has been applied to 12 of the 19 potentially toxic pollutants of interest including refractory forming elements, e.g., Ba, Ti, and V. This procedure, coupled with AAS, also has been applied to the analysis of granite, coal, coal ash, glass, and fish tissue for 18 elements and resulted in a relative standard deviation of approximately 5% for trace elements. The procedure has the following advantages: elimination of interelement and ionization interferences, elimination of volatilization and retention losses, relatively low cost per analysis because of the reduction in time and supervision required and the elimination of expensive platinum ware containers.

Since fewer interference problems occur with ICP than with AA procedures, the acid-pressure decomposition technique is directly applicable. In this method, the samples are decomposed in a Teflon cup and then encapsuled in a stainless steel bomb with a decomposition medium of hydrofluoric and nitric acid. The samples are digested for 0.5 to 3 hr at 370 K to 440 K. The higher temperature is used for samples of higher organic content.

Two methods of sample preparation were used for sampling the train solutions that had collected the volatile elements in flue gas. The first, used for the mercury determination, was the cold vapor technique. It included digestion with fresh acid-dichromate followed by reduction with hydroxyl amine (for excess permanganate) and stannous chloride. The second method was to treat a portion of the solution with sodium borohydride to form the hydrides of arsenic, selenium, and antimony prior to their determination by AAS using an argon/hydrogen/air flame with the sample entrained within it.

Elemental pollutants (anions): Fluorine and chlorine cannot be determined by AAS. Samples were analyzed for fluorides following digestion under pressure and absorbed in a sodium hydroxide medium.

After buffering, fluorides were determined with a fluoride-selective electrode. The practical limit of detection was 10 µg of fluoride per gram of sample. Chlorine was determined by igniting the samples in a bomb and titrating the aqueous washings with silver nitrate. The practical limit of detection was 0.01 to 0.03%.

Sulfates: Solid samples were extracted with hot water for 24 hours. Sulfates in liquid and extracts from solids were determined by microtitration with barium perchlorate using a Thorin indicator. Results are reported as water soluble sulfate as SO_4 .

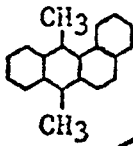
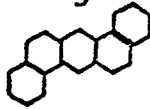
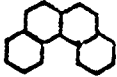
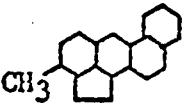

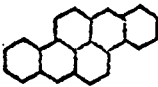
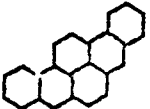
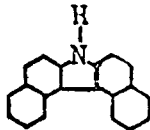
Organic pollutants: The organic compounds in the particulate matter were separated from the total particulate by extraction with benzene. The separated organic material and the organic material collected in the Na_2CO_3 or NH_4OH impingers and the Tenax plug were analyzed for POM.

POM: The POM in the benzene soluble fraction was separated from PCB, aliphatic and heterocyclic compounds by column chromatography with activated silica gel as the adsorbent.

Following the isolation of the total POM, gas chromatography with electron capture detection was used to quantify the individual POM. Solution detection limits were in the 0.2-0.5 µg/ml range. A Drexsil-300 packed column has been used to separate 70 POM.⁽³⁷⁾ This packing was used in the current program to separate the 8 POM's listed in Table 4-8. For the current program, quantification of 5 of the 8 desired POM's* was made by comparing sample peak areas with areas obtained from synthetic mixtures. Of the remaining 3 POM's, benzo[c]phenanthrene and dibenzo[a,h]pyrene could be identified by known relative retention times.⁽³⁷⁾ However, there was no information of GC analysis of dibenzo[a,g]carbazole on Dextsil-300, making identification impossible without a standard.

*Standards could not be obtained for benzo[c]phenanthrene, dibenzo[a,h]pyrene and dibenzo[c,g]carbazole.⁽²⁹⁾

TABLE 4-8. CARCINOGENIC POLYCYCLIC ORGANIC MATERIALS

Compound	Structure	Carcinogenicity
1. 7,12 Dimethylbenz[<u>a</u>]-anthracene		+ 4
2. Dibenz[<u>a,h</u>]anthracene		+ 3
3. Benzo[<u>c</u>]phenanthrene		+ 3
4. 3 Methylcholanthrene		+ 4
5. Benzo[<u>a</u>]pyrene		+ 3
6. Dibenzo[<u>a,h</u>]pyrene		+ 3
7. Dibenzo[<u>a,i</u>]pyrene		+ 3
8. Dibenzo[<u>c,g</u>]carbazole		+ 3

6001-48

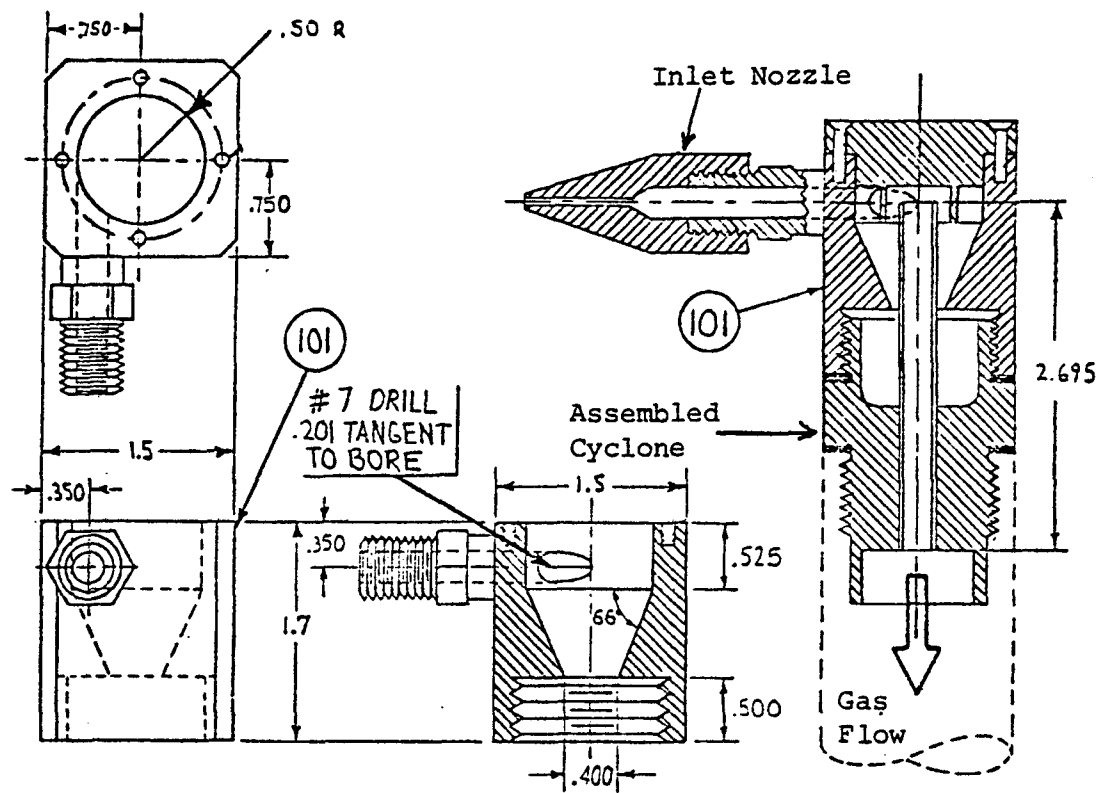
4.2.2 Quality Assurance of Analytical Methods

All samples were analyzed in duplicate to determine the precision of the analytical results. Selected samples of each type, for each unit tested, were fortified with three different concentrations to determine the accuracy of the analysis procedure. These experiments also determined the percentage of recovery for the digestion or extraction procedures. Where possible, standard reference materials from NBS were analyzed to determine accuracy of the procedures. All concentration determinations were taken from five-point calibration curves, which were repeated several times daily during the analysis of the samples. Samples were diluted or concentrated to bring them into the linear calibration range.

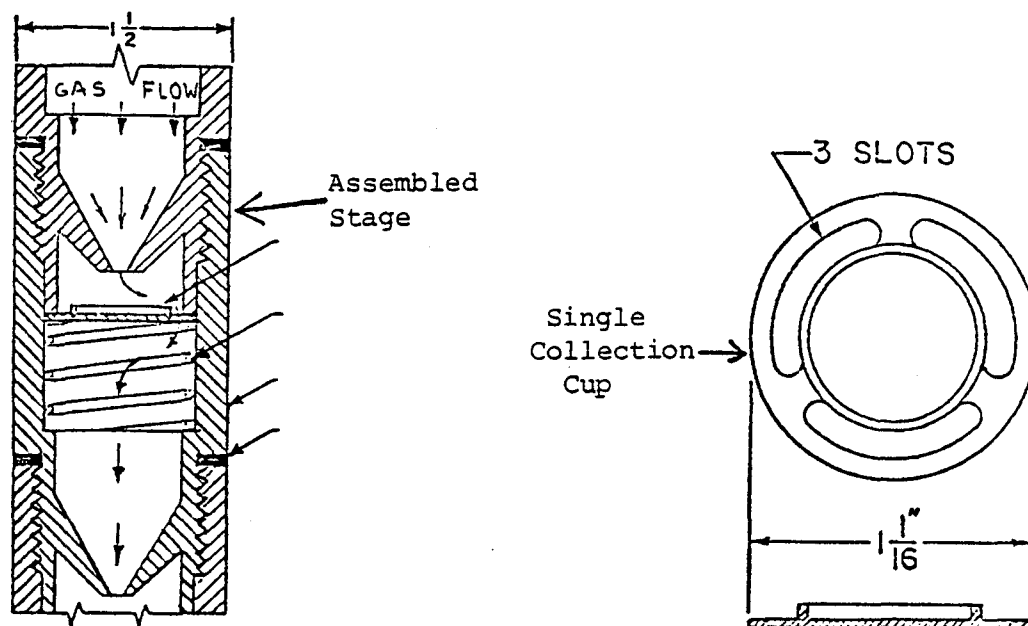
4.3 PARTICULATE SIZE

The particulate size was measured using a Brink Model "B" Cascade Impactor. A low volume type impactor was selected because the grain loading of the coal fueled boilers was relatively high. The nominal sample flow rate of 2.8 l/min (liters per minute) was low enough that the impactor did not readily overload. One stage of the cascade impactor and the precutter cyclone used with coal fuel are shown in Figure 4-8. The cyclone design was patterned after the Southern Research Institute Model SRI-4.⁽³⁸⁾

A Cahn Model G-2 Electro-balance with a sensitivity of 0.05 micrograms was used to weigh the collected sample. This sensitivity was needed for the lower stage of the impactor where the collected weight occasionally was less than 0.1 mg. To improve the accuracy of the weighing, an aluminum foil substratum was placed in each steel collection cup. The particles were collected and weighed on these lightweight cups, and the original steel collection cups were used only as a backing for the foil cups.



PRECUTTER CYCLONE



STAGE

Figure 4-8. Detail of one stage and of precutter cyclone for cascade impactor. 6001-48

A common problem with impactors is that the particles do not adhere to the stage surface, but strike it, rebound, and are reentrained in the flow through the slots down to the next stage. Reentrainment did not prove to be a problem with the cascade impactor measurements however. The flue gas flow rate was reduced from the nominal 2.8 l/min to 2.0 l/min or less, and visual examination of the collection stages by hand lens found no evidence of scouring or reentrainment. One set of stages was further examined under an electron microscope and there was no sign of a significant number of particulates that were larger than the aerodynamic diameter cut point of the preceding stage. There was, however, a considerable amount of sponge-like material that appeared to be an agglomeration of small particles.

Back-up filters were used as the final stage of the impactor to collect the material that passed the last impaction stage. Binderless, glass-fiber filter material, such as high-purity Gelman Type A Glass Fiber-Filter Webb was employed for this purpose. The 25 mm diameter circular filters were placed under the spring in the last stage of the impactor. The filter was protected from being cut by the spring by a Teflon O-ring, and a second filter disc and a wire mesh were placed beneath the filter to act as a support.

The flow rate and nozzle size were closely coupled, and requirements for isokinetic or near-isokinetic nozzle flow sometimes forced a compromise on nozzle selection. The order of priorities used by KVB in the field to determine the proper nozzle size was (1) nozzle diameter not smaller than 2 mm, (2) last stage jet velocity not excessive, (3) isokinetic sample collection rate, and (4) nozzle diameter (if greater than 2.0 mm). The impactor nozzle diameter was selected to provide as close to isokinetic collection as possible, but a nozzle bore less than 2 mm was avoided to forestall nozzle plugging by fly ash.

The impactor assembly was placed inside the stack and was heated to flue gas temperature by the flue gas itself before the sample collection was begun. The inlet nozzle was pointed downstream of the flow field during this heating phase to prevent the premature accumulation of particulates in the impactor.

The flow through the impactor was measured before each use to determine the actual cut points of the individual stages. This flow then was maintained by monitoring it with the pressure gauges on the EPA Method 5 control box. The pump on the control box was used to maintain the flow. During data analysis the true cut points were calculated for the actual gas flow rate through the impactor and cyclones using an approximate solution to the following two equations. ⁽³⁸⁾

$$D_{50} = 1.43 \times 10^4 \left[\frac{\mu D_c^3 P_s X(I)}{\rho_p Q_I P_o C 472.0} \right]^{1/2}$$

$$C = 1 + \frac{2L}{D_{50} \times 10^{-4}} \left[1.23 + 0.41 \text{ EXP } \left[(-0.44 D_{50})/L \times 10^{-4} \right] \right]$$

where

D_{50} is the stage cut point (μm),
nominal is 0.25, 0.5, 1.0, 1.5, and 2.5 μm ,

μ = gas viscosity (poise),

D_c = stage jet diameter (cm),

P_s = local pressure at stage jet (atm),

ρ_p = particle density (gm/cm^3),

Q_I = impactor flow rate (cfm),
nominal is 2.8 l/min, 46.7 cm^3/sec or 0.10 ft^3/min ,

P_o = ambient pressure at impactor inlet (atm),

C = Cunningham Correction Factor,

L = Gas mean free path (cm), and

$X(I)$ = Number of holes per stage.

Exact solution can be achieved by iterative methods.

The particle size reported can be either the aerodynamic diameter based on the behavior of unit density particles, or the approximate physical diameter based on the estimate of the true particle density. The aerodynamic diameter is reported as the particle size of unit density that is collected with 50% efficiency by the impactor stage. The symbol conventionally used for aerodynamic diameter is D_{50} . In either case, the particles are assumed to be spherical.

Measurements were made at a sufficient number of points across the flue or smoke stack, as specified by EPA Method 5, to make certain that a representative sample of particulates was obtained.

When coal fuel was fired the proportion of material with a size larger than ten micrometers was appreciable. The precutter cyclone shown in Figure 4-8 was used to collect this material and to prevent overloading of the upper impactor stages. The equations and nomenclature that were used to calculate the D_{50} , or cut point, for the cyclone was:⁽³⁸⁾

$$D_{50} = \sqrt{9\mu B_c / 2\pi N_c V_c (\rho_s - \rho)}$$

where

D_{50} = cyclone D_{50} (μm),

μ = gas viscosity (poise),

ρ_s = density of particle (g/cm^3),

ρ = gas density (g/cm^3),

N_c = number of turns made by gas stream in the cyclone body and cone,

V_c = inlet gas velocity (cm/sec), and

B_c = width of cyclone inlet (cm).

The square root relationship between D_{50} and V_c was used to calculate the aerodynamic diameter of the cyclone over the range of flowrates. It also was used to calculate the D_{50} 's of the individual stages of the impactor. Since the cyclone had been calibrated at a known flowrate, one can rewrite the equation as

$$D_{50}(1) \doteq \sqrt{C/V_1}$$

where

$D_{50}(1)$ = the cyclone cut point at flowrate 1, nominal is 7.3 μm

C = the cyclone calibration constant, and

V_1 = flowrate 1, nominal is 2.8 l/min, 46.7 cm^3/sec or 0.10 ft^3/min .

Then the relationship between $D_{50}(1)$ and $D_{50}(2)$, the cut points at the two different flowrates, was

$$D_{50}(2) \doteq D_{50}(1) \sqrt{V_1/V_2}$$

For particles of different mass densities, the nominal particle aerodynamic diameter was corrected using the relationship:

$$D(\rho_2) = D(\rho_1) \sqrt{\rho_1/\rho_2}$$

where

ρ_1 = the density of the calibration aerosol, (1.35 g/cc),

ρ_2 = the density of the test particulate (g/cc),

$D(\rho_1)$ = aerodynamic diameter of the calibration aerosol (μm)

$D(\rho_2)$ = aerodynamic diameter of the test particulate (μm)

The density of fly ash that was used in the calculation was taken from Reference 39 and was 1.78 g/cm^3 for particulates less than 44 μm in diameter.

These relationships have been verified experimentally, (38) and they were used to calculate the true aerodynamic diameters of the cascade impactor stages and cyclone.

All the material from the nozzle to the outlet of the cyclone was included with the cyclone catch. All material between the cyclone outlet and the second stage nozzle was included with material collected on the first collection substrate. All adjacent walls were brushed off, as well as around the underside of the nozzle. All material between the second stage nozzle and third stage nozzle was included with that on the second collection substrate. This process was continued down to the last collection substrate.

4.4 MATERIAL BALANCE

A mass balance calculation was done for the three coal-fired boilers where the emissions were analyzed for trace metal and organic content. The method of calculation is discussed in this section and the results of the calculations are discussed in the following sections. The input term to the balance was the quantity of a particular trace element that was found upon analysis to be in the coal burned during the test. The output terms were the amount of the element found in the bottom ash, the dust collector ash, and the fly ash in the flue gases.

Imbalance of the volatile elements will result if the flue gas is sampled infrequently, therefore, an attempt was made to collect enough data from three successive test runs that each material balance could be made three separate times. This technique would provide an expected range of material imbalance of 25% with 90% confidence, however, the goal of at least three test runs was not always achieved.

A practical field test problem with industrial boilers was to collect for measurement all of the solid material produced by the combustion process. During boiler operation, a significant quantity of material was deposited on the furnace bottom as refuse and slag, on the boiler tubes as slag and soot, and in the dust collector as ash. For the furnace bottom and dust collector, the

effect of differences in deposit rates during the test were minimized by emptying the collector before and after the test. If this plan was not practical, the collector was emptied one-half hour before the start of the test and again one-half hour before completion of the test. It was assumed that the quantity of ash would be the same as if the emptying had occurred at the beginning and end of the test and that the quantity of ash collected was equal to that actually produced during the test.

4.4.1 Fuel

Three fuel-related items must be considered in determining the input to the boiler. These items are fuel-feed rate, fuel sampling, and fuel analyses.

Fuel-Feed Rate: Few coal-fired industrial boilers were encountered that had facilities for conveniently determining fuel-feed rate by weight or any other technique. However, one of the requirements for trace species testing was that the coal feed rate be measured, and it was possible to find three boilers that did have a provision for weighing the amount of coal fed to the burners. An alternative method would have been to estimate the feed rate by a heat balance.

Fuel Sampling: ASTM D492-58, "Standard Method of Sampling Coals Classified According to Ash Content," gives guidelines for sampling, including recommended number of sampling increments and increment weight. However, coal sampling, like measuring coal firing rate, is very site dependent, and the exact technique used had to be tailored to each boiler after inspecting the facilities available at the boiler site. For the 11 to 12% ash, Group 1 coal that was used for the trace species tests, the standard method requires 35 incremental samples of two pounds each for a total weight of 70 pounds. To handle such a quantity of coal in the

field was impractical and a compromise was made. Twenty-five small incremental samples of a few ounces each were collected for a total sample weight of about two pounds.

Fuel Analysis: The coal was analyzed for its chemical and ash content and its heating value by Industrial Testing Laboratory, Kansas City, Missouri, as part of the trace species analysis of the collected sample. Proximate, ultimate and heat of combustion analyses on "as received" and "dry basis" were made and reported. The trace species content was determined by the Midwest Research Institute, Kansas City, Missouri.

4.4.2 Bottom Ash and Slag

Bottom ash and slag are the refuse that collects on the bottom of a furnace or is dumped into the ash pits by the action of the grate. As in the case of fuel, three items are important in defining the bottom ash from an industrial boiler: measuring the quantity of ash produced, collecting a representative sample, and analysis.

Accumulation Rate: The ash collector was emptied just prior to the start of a run and just after the end of a run and the contents weighed where this was possible. At Location 31, it was not possible in actual practice, because the refuse collection system was not readily accessible during operation. It consisted of a large number of closed pneumatic and hydraulic devices for collection and disposal that proved to be impracticable to empty individually in a short time.

Ash Sampling: A large number of small samples of refuse were collected and combined into a single composite sample for analysis, as was done for the coal sample.

Ash Analysis: A proximate analysis of the bottom ash was performed and reported by Industrial Testing Laboratory, and a trace element analysis was performed by the Midwest Research Institute.

4.4.3 Dust Collector Ash

Each of the test boilers had a dust collector or bag house for collecting fly ash from the flue gas stream. The three important factors needed to characterize the dust collection for achieving an overall mass balance were the rate at which collector ash was produced, the method of collecting a sample of the ash, and the analysis of the ash.

Accumulation Rate: Standard methods did not exist for determining the rate of accumulation of ash by the dust collector nor for obtaining samples of the ash, since these data generally were not of concern to the operator. Hence, we encountered no facilities specifically for measuring ash accumulation at the test sites. At Location 31, Test 169, particulate concentrations in the flue gas were measured, both upstream and downstream of the cyclone dust collector, and these data were used to determine the rate of fly ash accumulation in the dust collector. At Location 35, Test 166, measurements were made only at one point in the exhaust gas stream, as is explained in Section 6.

Collector Ash Analysis: A large number of small samples were collected and combined for analysis by the testing laboratory. The same analytical methods used for bottom ash analysis were used for analyzing collector ash for unburned carbon content, trace elements and organics.

4.4.4 Fly Ash

Both the solid particulates and the condensible particulates were included in the determination of the total fly ash concentration in the flue gas. For Tests 166 and 169 a standard EPA Method 5 analyzer was used. For the special reagent comparison tests, Tests 213 and 214, the trace species collection train pictured in Figure 4-1 was employed. The impinger case had been enlarged sufficiently to hold eight rather than four bubblers.

4.4.6 Soot

A salient difference between the ash measurements made as part of the trace species tests and conventional emission tests was that the soot generated during the test was collected and included in the analysis. The soot blowers were operated just prior to the start of a test to clear out the soot that had accumulated on the boiler tubes and walls. Just prior to the end of a test the soot blowers were operated again to dislodge the soot that had collected during the test.

SECTION 5.0

FIELD TEST, ORIGINAL COLLECTION TRAIN

The original design of the trace species train had been developed by field research and test teams that were under contract to the U.S. Environmental Protection Agency at the time the trace species testing was undertaken by KVB, Inc. This original design was used in the first KVB test at Location 29 and by the Midwest Research Institute at two of their test sites.⁽⁴²⁾ Reagents initially used by KVB consisted of distilled water in the first two impingers, saturated sodium carbonate in impinger 4, and sulfuric acid permanganate in impingers 5 and 6. MRI used these and other reagents. A fiber filter and Tenax adsorbent were used between impingers 3 and 4. Because the vaporous mercury was not being properly scrubbed out of the stack gas, the results were not considered to be satisfactory.

The basic mechanical design of the collection train did not change significantly during the first two KVB tests. Bubblers were substituted for impingers so the gas could be pumped through the train at isokinetic speeds. The Tenax adsorber holder was changed from a cylinder to a high-cross section spherical shape and the bubbler chemicals were changed several times.

Four test runs were conducted at Location 30, two for inorganic collection and two for organics. Reagents for the inorganics tests were sodium carbonate in impingers 1 and 2, acid-dichromate in impingers 4 and 5, and acid-permanganate in impinger 6. Nitric acid was used in one test and sulfuric acid in the second. The results showed that selenium was collected in the first impinger, antimony in the first two, arsenic in the two dichromate impingers (4 and 5) and mercury in all five, but highest in the permanganate (6). Other tests by MRI indicated mercury collection efficiency was still low.⁽⁴²⁾ For organics tests, toluene was used in the last two impingers and a second Tenax adsorber replaced impinger 4.

From the results of the tests at Locations 29 and 30 and by MRI, the sampling reagents shown in Figure 5-1 were recommended by MRI for future tests by KVB. The function of the two sodium carbonate-water bubblers was to trap PCB's, selenium and antimony, and to maintain a pH high enough to stabilize benzo[a]pyrene. This solution also served to trap SO_x , thus protecting oxidizing bubblers later in the train as well as producing an oxidizing solution for selenium and antimony vapor. The empty bubbler was necessary to catch spray from the preceding bubbler.

A single holder containing a Tenax adsorber was placed between the third and fourth bubblers, rather than the combination of a fiber filter and Tenax that formerly had been used in this position. With this arrangement, including a larger amount of Tenax and 200 ml of reagent in the bubblers, a serious pressure drop could be avoided. After the Tenax, the remainder of the recommended train was as follows: two 10% nitric acid 5% sodium dichromate bubblers, followed by one 10% nitric acid potassium permanganate bubbler, an empty bubbler for spray from the permanganate and finally a dry bubbler with silica gel. This mass train configuration was expected to give a good compromise between collection of POM and volatile metals.

Problems were still considered to exist with this recommended reagent configuration, primarily the inability to assure high percentage collection of mercury vapor at isokinetic flow rates.⁽⁴²⁾ As a result, this reagent set was abandoned without further test and an alternate set of reagents was adopted as recommended by EPA. The sodium carbonate was replaced with ammonium hydroxide in the first two bubblers. A mixture of hydrogen peroxide, silver nitrate, and nitric acid was used in bubblers 4, 5 and 6. The subsequent test at Location 35, discussed in the next section, revealed that ammonium hydroxide caused the Tenax to plug. The ammonium hydroxide was then replaced with sodium carbonate. This reagent set was used for all subsequent tests with this particular sampling train.

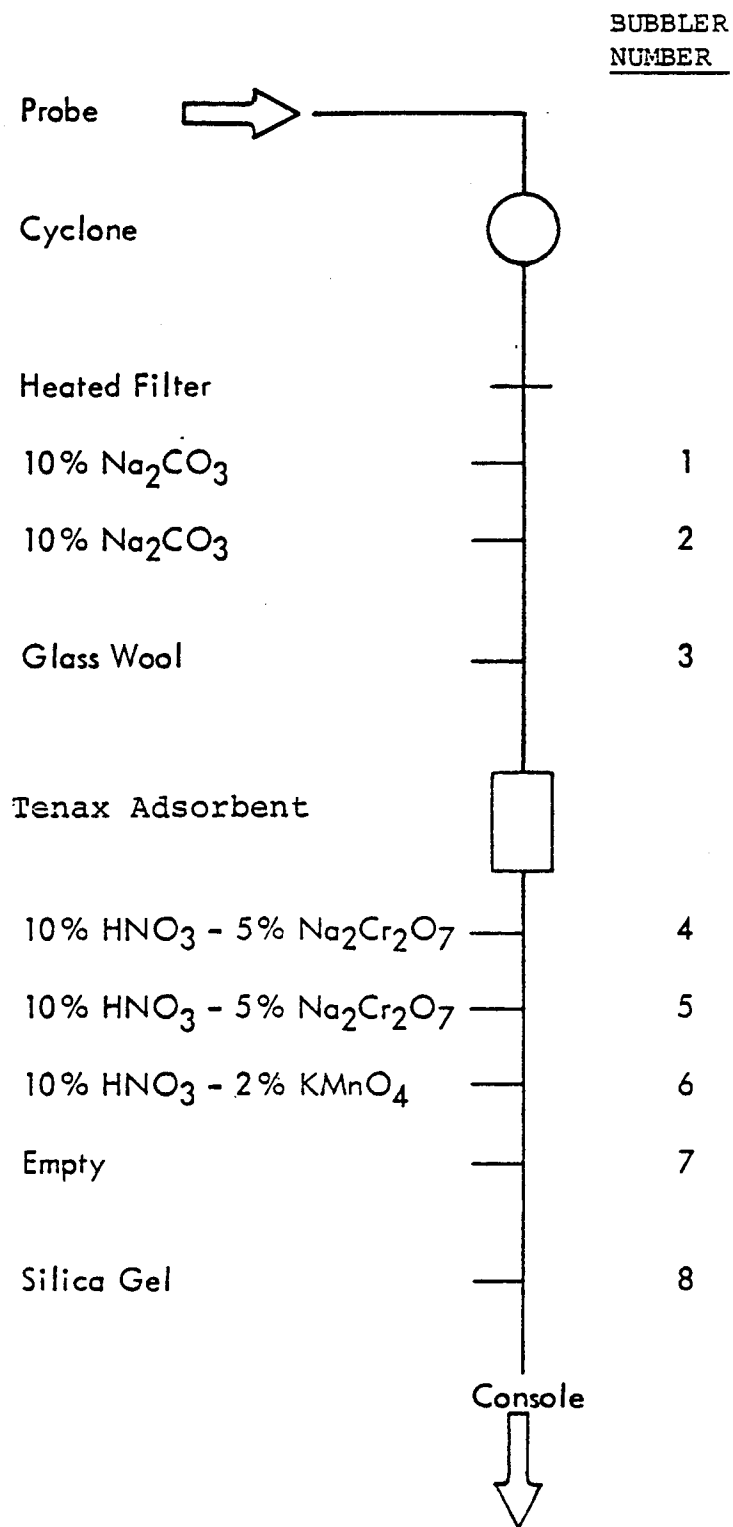


Figure 5-1. Reagent set recommended following initial tests.

6001-48

SECTION 6.0

FIELD TEST NO. 166, MODIFIED COLLECTION TRAIN

Material balances of the elements for the three runs of Test 166 at Location 35 on a chain grate stoker firing crushed coal are shown in Figure 6-1. The mass of an individual element collected is the mass found upon analysis in the combined furnace bottom and dust collector ashes and in the flue gas fly ash. The balance also includes the amount of arsenic, mercury and selenium that was present in the stack gas as a vapor.

In general, the moderately-volatile elements, such as barium and manganese, tended to concentrate in the hopper ashes, and the proportion recovered was high, running from 50% to 260% of the amount of the element that was in the coal.

The recovery of mercury was near 100% in all three runs. This high recovery was gratifying because it had been difficult to capture mercury heretofore. However, almost all of the mercury was recovered in the furnace bottom and the dust collector ashes from the ash hopper, and only about four percent was recovered from the stack gas vapor by the bubbler reagents. Other investigators have found up to 90% of the mercury to be in the stack gas as a vapor. This discrepancy leads one to suspect that the reported concentrations of mercury in the hopper ash are in error on the high side.

The recovery of the other two highly volatile elements, arsenic and selenium was only about 40%, but they too were found predominately on the hopper ashes and not in the stack gas as a vapor. However, the low recovery from the stack gases may have been due to the bubbler chemicals not effectively scrubbing out the arsenic and selenium.

Mass of element collected/Mass of element in coal, %

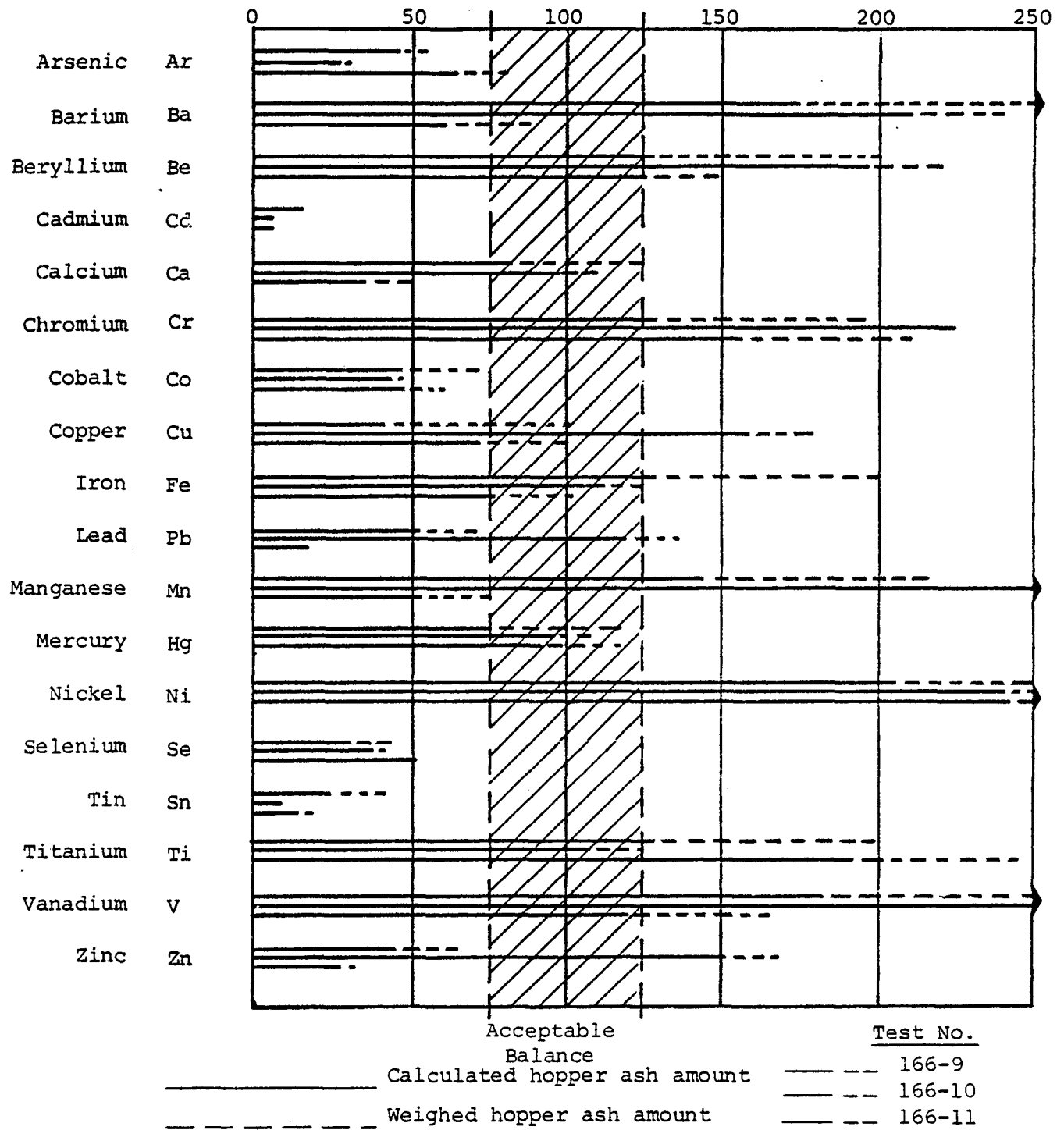


Figure 6-1. Material balance test run numbers 166-9, 166-10, and 166-11.

The elements, chromium, nickel, and titanium, were much overbalanced. The surplus of these elements possibly was due to contamination from the stainless steel sample intake nozzle or the steel from which the boiler itself was made.

The results of the material balance depended upon whether a measured or a calculated amount of hopper ash was used for the computation. The calculated amount of bottom and collector ash was a good deal higher than the amount of ash contained in the coal, since the hopper ash contained from 40% to 70% of carbon and other volatiles. The amount of ash removed from the hopper and weighed was 11% to 54% higher in turn, than the calculated ash. Since it was difficult to get an uncontaminated sample of the hopper ash and there was considerable uncertainty about the weights, two calculations were made, one for the calculated hopper ash and another for the measured hopper ash.

The material balance based on the calculated hopper ash is shown in Figure 6-1 by the solid bar and the one based on the measured hopper ash is shown by the dashed extension to the solid bar. The actual balance probably lies between the end of the solid bar and the end of the dashed bar.

Making a complete material balance for chloride and fluoride was not possible because there was an insufficient quantity of the flue gas fly ash for analysis. A partial balance for these two species is shown in Table 6-1 for each of the runs of Test 169.

An acceptable balance was achieved for chloride for two out of the three runs, while the fluoride balance was successful only for run number 10. Apparently a sizable proportion of the fluoride vapor was not condensed by the reagents in the bubblers. About three-quarters of the chloride that was captured was in the furnace bottom and dust collector ashes in the hopper. It tended to partition out with the heavy particulate. The fluoride, on the other hand, was distributed relatively uniformly between the hopper ash and the stack gas vapor.

TABLE 6-1. CHLORIDE, FLUORIDE AND SULFATE MATERIAL BALANCE
Test No. 166, Location No. 35

Run No.	In Coal g %	In Measured Hopper Ash g %	In Stack Gases				Total and Balance	
			Particulate g %		Vapor g %		g	%
9 Chloride	9,065 100	5,302 58	insufficient sample		1,910	21	7,212	80 *
10	10,756 100	754 7	insufficient sample		2,601	24	3,355	31 *
11	6,497 100	5,107 79	insufficient sample		1,656	25	6,763	104 *
9 Fluoride	1,877 100	347 18	insufficient sample		711	38	1,058	56 *
10	1,137 100	520 46	insufficient sample		657	58	1,177	104 *
11	1,081 100	339 31	insufficient sample		438	41	777	72 *
9 Sulfate †	80,217 100	16,950 21	38.4	0.05	790,990	986	807,978	1,007
10	83,952 100	36,922 44	35.2	0.04	1,120,388	1,335	1,157,345	1,379
11	54,047 100	23,679 44	5.27	0.01	961,260	1,778	984,944	1,822

* Partial balance only, insufficient particulate sample for total balance.

[†] Sulfate in solids is water soluble sulfate as SO_4 .
Sulfate in stack gas vapor includes all sulfur compounds collected, expressed as SO_4 .

The sulfate collected in the hopper ash and stack gas particulates was 21 to 44% of the sulfate present in the coal. Sulfate reported for stack gas vapors includes all sulfur compounds collected in the first two impingers in the sample train. Any SO_2 or SO_3 present in the gas will be indicated as sulfate.

Some of the polycyclic organic materials (POM's) were found in the coal and in the hopper ashes. The emissions of these organics are tabulated in Table 6-2. POM numbers 1 and 2 were detected in the hopper ash but not in the stack gas. The presence of POM in the hopper ash was unexpected, since the melting and/or subliming temperature of these organics is only about 475 K and well below the temperature of the combustion gases. The sample of fly ash collected from the stack gas was of insufficient size for analysis. In future tests of this type, provision should be made to collect a larger sample of the stack gas particulate.

6.1 BOILER AND FUEL CHARACTERISTICS

Boiler #6 at Location 35 was an Erie City Iron Works brand watertube boiler installed in 1960. The superheated steam boiler had a rated capacity of 227 GJ/hr (215,000 lb/hr) of equivalent saturated steam flow and final steam conditions of 755 K (915°F), and 6.13 MPa (875 psig). The boiler was coal fired with a chain-grate, traveling-type stoker manufactured by Combustion Engineering. Forty-six overfire air nozzles designed to enhance mixing of the fuel and combustion air were mounted above the chain grate, and air was supplied to these nozzles by a separate overfire air fan. Primary combustion air was supplied to the windbox under the grate by a forced draft fan. An induced draft fan maintained a balanced furnace draft. A tubular air preheater heated the combustion air to approximately 500 K (220°F).

The boiler load was limited to approximately 60% of rated capacity during the test program due to undersized fans and blocked gas passages. Consequently, the test load was established at 110 GJ/hr

TABLE 6-2. ORGANICS EMISSIONS
Test No. 166, Location No. 35

Run No.	POM No.	Name	In Coal g %		In Hopper Ash g %		In Stack Gases			
							Particulate		Vapor	
							g	%	g	%
9	1.	7,12 Dimethylbenz[a]anthracene	none		none		insufficient		none	
			detected		detected		sample		detected	
10			none		2.26	-	insufficient		trace	
			detected				sample			
11			none		1.39	-	insufficient		none	
			detected				sample		detected	
9	2.	Benzo[a]pyrene	109	100	37	34	insufficient		none	
							sample		detected	
10			245	100	92.6	38	insufficient		none	
							sample		detected	
11			18.8	100	651	3462	insufficient		none	
							sample		detected	
9	3.	3 Methylcholanthrene	none		none		insufficient		none	
			detected		detected		sample		detected	
10			none		none		insufficient		none	
			detected		detected		sample		detected	
11			none		none		insufficient		none	
			detected		detected		sample		detected	
9	4.	Dibenz[a,h]anthracene	610	100	none		insufficient		none	
					detected		sample		detected	
10			822	100	none		insufficient		none	
					detected		sample		detected	
11			673	100	none		insufficient		none	
					detected		sample		detected	

(104,000 lb/hr) of equivalent saturated steam. Figure 6-2 is a schematic of the boiler. The three sampling ports are shown in the vertical flue on the upper right side of the schematic just before the flue gas enters the horizontal breeching leading to the stack.

The characteristics of the boiler, the coal burned and the hopper ash collected during the three trace species tests are listed in Table 6-3. The load varied during from about 100 to 110 GJ/hr during the testing, and the excess oxygen listed of 10.8% is an average value for these tests. The hopper ash is the combined ash from the furnace bottom and the dust collector. All of these ashes were collected in a hopper beneath the boiler and removed periodically by running them into dump trucks. As the section of the table labeled "Hopper Ash Proximate Analysis" indicates, a relatively large proportion of the hopper ash was other than inert ash from the coal, and the hopper ash had a significant heat of combustion. Consequently, a good deal more "ash" was collected from the hopper than originally went into the boiler as ash in the coal.

In comparison to other coal stoker units, the nitrogen oxides emissions of 124 ng/J from this boiler were unusually low, since the average nitrogen oxides emissions from all coal-fired boilers tested during this program was 290 ng/J. The pollutant emissions during the trace species test 166-11 are summarized below. During the testing the load varied between 100 and 110 GJ/hr.

Load, GJ/hr (10^3 lb/hr)	100-110	(95-104)
Total nitrogen oxides, ng/J (ppm)	124	(203)
Carbon dioxide, %	7.2	
Carbon monoxide, ng/J (ppm)	32	(85)

One of the contributing factors to the reduced nitrogen oxides emissions was the low-intensity, desultory flame. Also, since the testing necessarily was conducted at relatively low loads and the heat absorption area of the unit was comparatively large, the products of

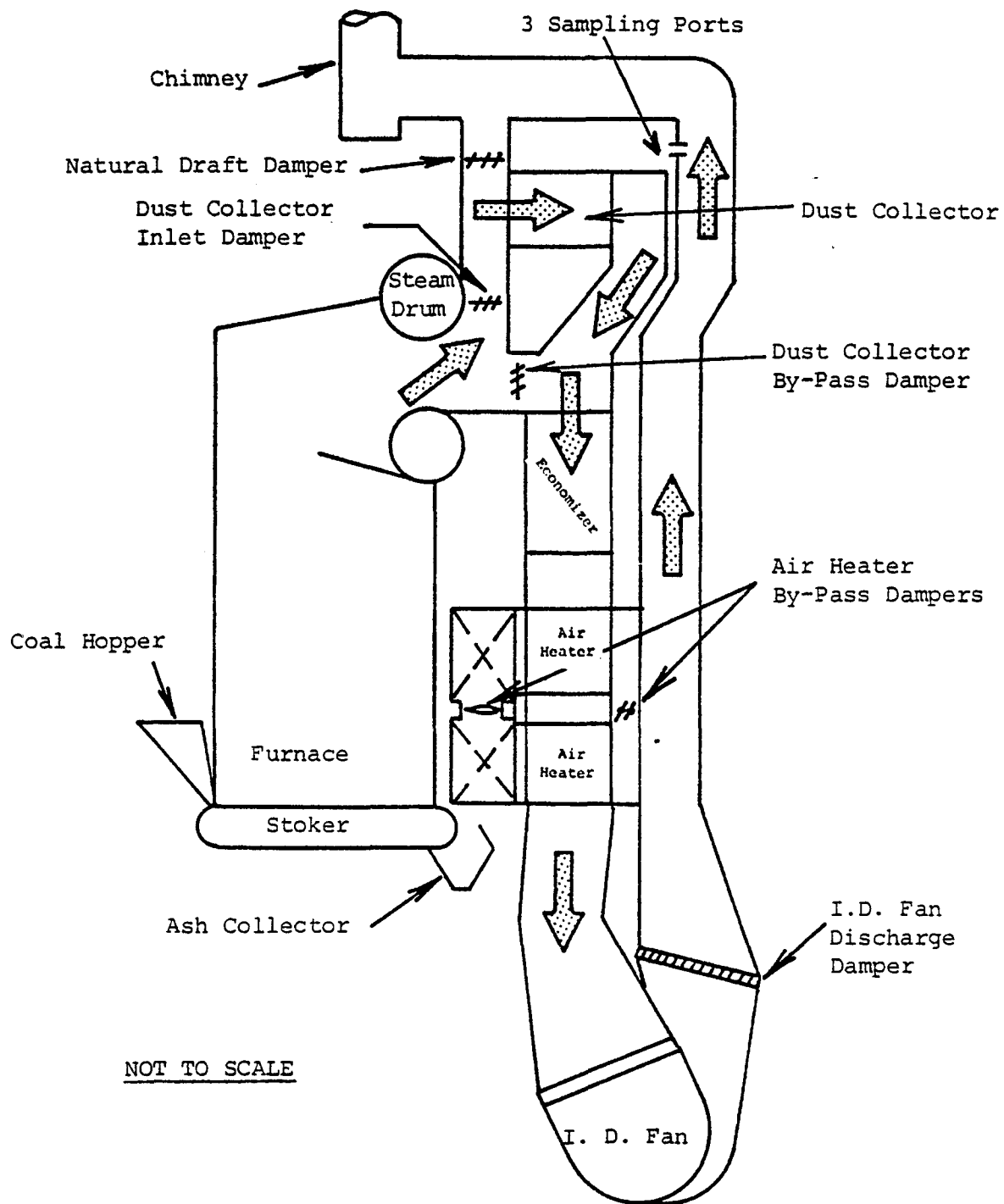


Figure 6-2. Boiler schematic showing gas flow paths and sampling port location.

6001-48

TABLE 6-3. BOILER, COAL, AND ASH CHARACTERISTICS
Location No. 35

Test No.	166-9	166-10	166-11
Date, 1975	April 7	April 8	April 9
Fuel Type	Crushed Coal	Crushed Coal	Crushed Coal
Burner Type	Chain grate	Chain grate	Chain grate
Test Load, GJ/hr (10 ³ lb/hr)	100 - 110 (95 - 104)	100 - 110 (95 - 104)	100 - 110 (95 - 104)
Average Excess Oxygen, %	10.8	10.8	10.8
Coal Burned kg (lb)	16023 (35251)	17490 (38478)	11030 (24266)
Test Duration sec (min)	8100 (135)	8100 (135)	5400 (90)

Coal Proximate Analysis

AS RECEIVED:			
Moisture, %	4.11	4.19	4.17
Ash, %	12.46	12.32	16.33
Volatile Matter, %	38.08	38.35	36.72
Fixed Carbon, %	45.35	45.14	42.78
Sulfur, %	2.81	3.23	3.10
Heat of Combustion, J/g (Btu/lb)	27,173 (11,685)	27,341 (11,757)	25,992 (11,177)
DRY BASIS:			
Ash, %	12.99	12.86	17.04
Volatile Matter, %	39.71	40.03	38.32
Fixed Carbon, %	47.30	47.11	44.64
Sulfur, %	2.93	3.37	3.23
Heat of Combustion, J/g (Btu/lb)	28,339 (12,181)	28,536 (12,271)	27,122 (11,663)

Hopper Ash Proximate Analysis

Moisture, %	1.16	1.76	1.04
Ash, %	55.39	31.52	58.89
Volatiles, %	4.01	5.32	4.30
Fixed Carbon, %	39.44	61.40	35.77
Sulfur, %	1.58	2.98	1.79
Heat of Combustion, J/g (Btu/lb)	20,190 (6,203)	22,197 (9,545)	13,330 (5,732)

6001-48

combustion were cooled rapidly. The combination of low intensity combustion, low firing rate and a large furnace would be expected to result in low nitrogen oxides emissions. The baseline solid particulate emissions were only 133 ng/J ($0.315 \text{ lb}/10^6 \text{ Btu}$) and were relatively low compared to the sixteen other coal-fired boilers that were tested during the combustion modification part of the Program (see Figure 7-2, Test No. 165 in the following section of this report).

6.2 COLLECTION TRAIN

After consideration of the results of the prior trace species sample collections made at Locations 29 and 30, an ammonium-hydroxide-based reagent was provided to KVB for bubblers 1 and 2. It was expected that with this reagent one could pump at the higher rate necessary for isokinetic sample collection and still scrub out the mercury. When the ammonium-hydroxide-based reagent was used, however, the trace species train repeatedly plugged up, because the granular Tenax adsorbent became hygroscopic and stopped the flow of exhaust gas through it.

The Tenax adsorbent had not picked up water heretofore. A number of special test runs and consultations resulted in the conclusion that the cause was the new reagent used to trap the mercury. The flue gas at Location 35 had such a high sulfur content that it was necessary for the field test crew to wear gas masks when in the area of the test ports. Apparently, the sulfur in the flue gas reacted with the ammonium hydroxide in the first two bubblers and formed an ammonium-sulfur compound that caused the Tenax to become hygroscopic. As the Tenax became wet, it no longer was granular and the flue gas could not be pumped through it.

The EPA Project Officer's representative then directed KVB, Inc. to use a sodium carbonate-based reagent in the first two bubblers. With the sodium carbonate reagent the trace species tests were run with no further delay. The contents of the eight bubblers that finally were selected were the following:

Bubbler No. 1	2% sodium carbonate in water
Bubbler No. 2	2% sodium carbonate in water
Bubbler No. 3	dry
Adsorbent	Tenax
Bubbler No. 4	10% HNO_3 + H_2O_2 + AgNO_3 in water
Bubbler No. 5	10% HNO_3 + H_2O_2 + AgNO_3 in water
Bubbler No. 6	10% HNO_3 + H_2O_2 + AgNO_3 in water
Bubbler No. 7	dry
Bubbler No. 8	silica gel

The trace species collection train configuration that was used was that discussed and pictured in Section 3 of this report. The three test runs that are listed below were made using the sodium carbonate-based scrubbing reagent.

Test Run No.	166-9	166-10	166-11
Test Duration, min	135	135	90
Actual flow rate through train, cm^3/sec (ft^3/min)	171.4 (0.3632)	209.9 (0.4448)	314.7 (0.6667)
Actual volume through train, m^3 (ft^3)	1.388 (49.03)	1.701 (60.05)	1.700 (60.00)

6.3 SPECIES CONCENTRATION

Concentrations of the individual trace species that were found to be in the coal, in the combined furnace bottom and dust collector ashes and in the flue gas as fly ash are listed in Tables 6-4, 6-5, and 6-6. Concentrations of antimony could not be determined because of a chemical interference. The second part of each table lists the mass of the more volatile species, the organics and the sulfates that were scrubbed out of the flue gas stream by the bubblers and Tenax adsorbent of the trace species train. Bubbler reagents were analyzed only for the more volatile species and the organics.

Mercury balances are based on an assumed average mercury content in the coal of $0.15 \mu\text{g/g}$. Analysis of the coal indicated a mercury content of less than $0.3 \mu\text{g/g}$. The assumed average of $0.15 \mu\text{g/g}$, one-half the detectable limit, is a typical average for general coal types as indicated in Figure 3-1. (23)

TABLE 6-4. SPECIES CONCENTRATION
 Test No. 166-9, Location No. 35
 Coal, Furnace Bottom and Dust Collector Ashes, and Flue Gas Fly Ash

Species	Location of Species		
	Coal Fuel ($\mu\text{g/g}$)	Hopper Ash ($\mu\text{g/g}$)	Flue Gas Fly Ash ($\mu\text{g/g}$)
Antimony	Could not be analyzed - chemical interference		
Arsenic	6.0	11.4	250
Barium	39	108	283
Beryllium	1.1	3.2	20
Cadmium	2.4	0.1	10
Calcium	3,000	4,800	19,000
Chromium	15	101	250
Cobalt	2.3	4.3	13
Copper	25	77	270
Iron	15,000	49,000	160,000
Lead	8.5	1.8	131
Manganese	25	61	125
Mercury	<0.3	0.5	1.2
Nickel	4.6	37	100
Selenium	6.5	7.0	280
Tin	1.4	0.7	7.2
Titanium	790	6,600	7,400
Vanadium	54	280	625
Zinc	30	20	500
Chloride	565	1,100	*
Fluoride	117	72	*
POM 1†	†	†	*
POM 2†	6.8	10.4	*
POM 3†	†	†	*
POM 4†	38	†	*
Sulfate §	5,000	4,800	500

* Insufficient sample for analysis

Continued

† None detected

‡ POM 1: 7,12 Dimethylbenz[a]anthracene; POM 2: Benzo[a]pyrene; POM 3: 3 Methylcholanthrene; POM 4: Dibenz[a,h]anthracene

§ Sulfate is water soluble sulfate as SO_4 .

6001-48

TABLE 6-4. (Continued)
Test No. 166-9
Flue Gas Vapors

Species	Bubbler Number					
	1 Na ₂ CO ₃ (µg)	2 Na ₂ CO ₃ (µg)	Tenax (µg)	4 H ₂ O ₂ (µg)	5 H ₂ O ₂ (µg)	6 H ₂ O ₂ (µg)
Antimony	0.2	0.4	§	<0.5	<1.0	<1.0
Arsenic	11.4	3.3	§	<3	<7	<7
Mercury	<0.3	<0.3	§	0.1	<0.1	<0.1
Selenium	56	4.1	§	0.17	0.26	0.29
Chloride	21,000	2,900	§	§	§	§
Fluoride	7,300	1,600	§	§	§	§
POM 1†	†	†	†	§	§	§
POM 2†	†	†	†	§	§	§
POM 3†	†	†	†	§	§	§
POM 4†	†	†	†	§	§	§
Sulfate #	9.2x10 ⁶	0.7x10 ⁶	§	§	§	§

* Insufficient sample for analysis

† None detected

† POM 1: 7,12 Dimethylbenz[a]anthracene; POM 2: Benzo[a]pyrene;
† POM 3: 3 Methylcholanthrene; POM 4: Dibenz[a,h]anthracene

§ Not analyzed for

Sulfate includes all sulfur compounds collected expressed as SO₄.

TABLE 6-5. SPECIES CONCENTRATION
Test No. 166-10, Location No. 35
Coal, Hopper Ash and Flue Gas Fly Ash

Species	Location of Species		
	Coal Fuel (µg/g)	Hopper Ash (µg/g)	Flue Gas Fly Ash (µg/g)
Antimony	Could not be analyzed - chemical interference		
Arsenic	7.9	4.0	110
Barium	28	150	290
Beryllium	1.0	5.0	26
Cadmium	1.1	0.2	14
Calcium	2,200	5,200	17,000
Chromium	20	100	280
Cobalt	2.1	2.1	11
Copper	42	170	340
Iron	19,000	53,000	130,000
Lead	8.6	25	129
Manganese	26	170	144
Mercury	<0.3	<0.7	1.0
Nickel	6.1	37	124
Selenium	6.7	5.0	110
Tin	3.4	0.4	11
Titanium	764	2,050	7,550
Vanadium	50	320	645
Zinc	34	119	982
Chloride	615	1,100	*
Fluoride	65	69	*
POM 1†	†	0.3	*
POM 2†	14	12.3	*
POM 3†	†	†	*
POM 4†	47	†	*
Sulfate #	4,800	4,900	400

* Insufficient sample for analysis

Continued

† None detected

‡ POM 1: 7,12 Dimethylbenz[a]anthracene; POM 2: Benzo[a]pyrene;
POM 3: 3 Methylcholanthrene; POM 4: Dibenz[a,h]anthracene

§ Not analyzed for

Water soluble sulfate as SO₄.

6001-48

TABLE 6-5. (Continued)
 Test No. 166-10, Location No. 35
 Flue Gas Vapors

Species	Bubbler Number					
	1 Na ₂ CO ₃ (µg)	2 Na ₂ CO ₃ (µg)	Tenax (µg)	4 H ₂ O ₂ (µg)	5 H ₂ O ₂ (µg)	6 H ₂ O ₂ (µg)
Antimony	<0.1	0.2	§	<1.0	<1.0	<0.3
Arsenic	0.7	2.5	§	<6	<6	<6
Mercury	<0.2	<0.2	§	0.3	<0.1	<0.1
Selenium	31	2.8	§	0.03	0.03	0.01
Chloride	26,000	700	§	§	§	§
Fluoride	6,100	648	§	§	§	§
POM 1†	†	†	0.001	§	§	§
POM 2†	†	†	†	§	§	§
POM 3†	†	†	†	§	§	§
POM 4†	†	†	†	§	§	§
Sulfate #	11x10 ⁶	0.5x10 ⁶	§	§	§	§

* Insufficient sample for analysis

† None detected

‡ POM 1: 7,12 Dimethylbenz[a]anthracene; POM 2: Benzo[a]pyrene;
 POM 3: 3 Methylcholanthrene; POM 4 Dibenz[a,h]anthracene

§ Not analyzed for

Sulfate includes all sulfur compounds expressed as SO₄.

6001-48

TABLE 6-6. SPECIES CONCENTRATIONS
 Test No. 166-11, Location No. 35
 Coal, Hopper Ash and Flue Gas Fly Ash

Species	Location of Species		
	Coal Fuel (µg/g)	Hopper Ash (µg/g)	Flue Gas Fly Ash (µg/g)
Antimony	Could not be analyzed - chemical interference		
Arsenic	5.4	3.9	250
Barium	50	305	470
Beryllium	1.1	4.9	23
Cadmium	0.7	0.1	14
Calcium	2,200	6,200	19,000
Chromium	23	100	490
Cobalt	2.3	3.6	18
Copper	22	50	301
Iron	19,000	89,000	140,000
Lead	4.3	5.1	185
Manganese	20	100	139
Mercury	<0.3	0.4	<3
Nickel	6.4	46	203
Selenium	7.1	4.8	150
Tin	1.0	0.81	12.3
Titanium	886	4,100	6,100
Vanadium	50	330	630
Zinc	26	29	856
Chloride	589	1,100	*
Fluoride	98	73	*
POM 1†	†	0.3	*
POM 2†	1.7	59	*
POM 3†	†	†	*
POM 4†	61	†	*
Sulfate #	4,900	5,100	100

Continued

* Insufficient sample for analysis

† None detected

+ POM 1: 7,12 Dimethylbenz[a]anthracene; POM 2: Benzo[a]pyrene;
 + POM 3: 3 Methylcholanthrene; POM 4: Dibenz[a,h]anthracene

§ Not analyzed for

Water soluble sulfate

6001-48

TABLE 6-6. (Continued)
 Test No. 166-11, Location No. 35
 Flue Gas Vapor

Species	Bubbler Number					
	1 Na ₂ CO ₃ (µg) ³	2 Na ₂ CO ₃ (µg) ³	Tenax (µg)	4 H ₂ O ₂ (µg) ²	5 H ₂ O ₂ (µg) ²	6 H ₂ O ₂ (µg) ²
Antimony	<0.1	<0.1	§	<1.0	<1.2	<0.5
Arsenic	2.5	7.9	§	<6	<8	<3
Mercury	0.5	0.1	§	<0.1	<0.1	<0.1
Selenium	56	1.2	§	0.09	0.20	0.01
Chloride	24,000	1,500	§	§	§	§
Fluoride	6,100	650	§	§	§	§
POM 1†	†	†	†	§	§	§
POM 2†	†	†	†	§	§	§
POM 3†	†	†	†	§	§	§
POM 4†	†	†	†	§	§	§
Sulfate #	11x10 ⁶	3.8x10 ⁶	§	§	§	§

* Insufficient sample for analysis

† None detected

+ POM 1: 7,12 Dimethylbenz[a]anthracene; POM 2: Benzo[a]pyrene;
 + POM 3: 3 Methylcholanthrene; POM 4: Dibenz[a,h]anthracene

§ Not analyzed for

Sulfate includes all sulfur compounds expressed as SO₄.

SECTION 7.0

FIELD TEST NO. 169, MODIFIED COLLECTION TRAIN

7.1 TEST RESULTS

The results of the material balance for Test Run 169-3 at Location 31 on a boiler burning pulverized coal are shown in Figure 7-1. The mass of the individual element collected in the boiler is the sum of the masses found in the furnace bottom, dust collector and flue gases, both as particulate and vapor.

Most of the moderately-volatile elements, such as barium and manganese, concentrated in the bottom and collector ashes, and the recovery was at least 80% of the material input with the coal.

The more highly-volatile elements, such as arsenic and zinc, were not recovered either as ash or as vapor. The recovery was only 10% to 40% of the material originally contained in the coal.

One exception was vanadium. In both this test and in Test 166 discussed previously the recovery was high, from 88% to 120% of the vanadium in the coal. Forty-two percent of the vanadium that was recovered came from the collector ash. Another twenty-six percent was recovered from the flue gas fly ash. The vanadium tended to collect in the dust collector ash, rather than in the bottom ash, which is consistent with its being between moderately- and highly-volatile.

The collection of highly volatile mercury was only 40% of the quantity input with the coal and was much lower than the 100% recovery of Test 166. There was no apparent reason why this particular test should have been less successful in collecting mercury, since the same collection train and procedures were used for both tests.

The amount of the elements in the bottom ash was based on a calculated amount of bottom ash that was generated. It was not practical to measure the bottom ash, so the amount was taken to be the difference between the ash in the coal and the amount in

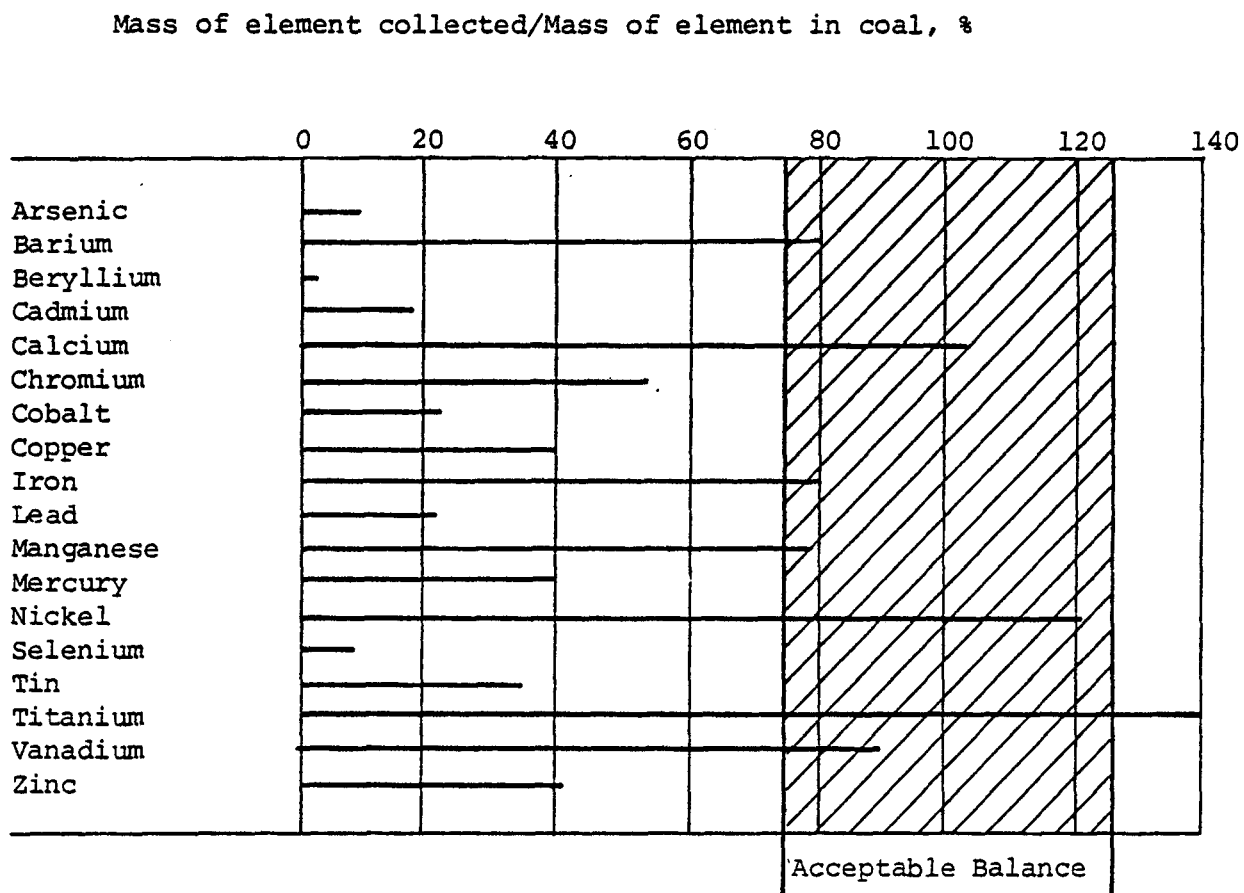


Figure 7-1. Material balance, test run no. 169-3.

the flue gas upstream of the dust collector. A correction was made to account for the fact that the ash actually contained only about 95% inerts.

As with Tests 166, 213 and 214 more nickel and titanium were collected than was contained in the coal. This surplus of nickel and titanium was deemed to have come from the stainless steel sample nozzle on the collection probe even though the nozzle was very short. If it had come from corrosion of the metal parts of the furnace, then the iron also should have been overbalanced. However, the amount of iron ran from 80% to 100% of the amount in the coal, and thus it appeared that corrosion of the boiler tubes was not a significant source of the nickel and titanium that were recovered.

It was not possible to make a complete material balance for chloride and fluoride because there was an insufficient sample of particulate in the flue gas downstream of the collector. The quantities determined are shown in Table 7-1.

Only 11 to 26 percent of the chloride and fluoride that was in the coal was recovered from the ashes and stack gas. Apparently, these two species passed through the boiler almost entirely in a vapor form. The recovery during Test 169 was much less than the 31 to 104 percent recovery that had been achieved previously during Test 166 as is shown in Table 6-1. Since the collection reagents in the bubblers were the same in both instances, the reason for the low recovery during the current test is unknown. The dearth of chlorides and fluorides in the bubbler reagents may have been due to the formation of free chlorine and fluorine and of hydrochloric and hydrofluoric acids. None of these four species would have been scrubbed out in any significant quantity by the 2% sodium carbonate solution in the first two bubblers nor by the chemical mixture in the fourth, fifth, and sixth bubblers. While the foregoing rationalization appears sound, the reason why it did not apply also to the earlier Test 166 is unclear at present.

TABLE 7-1. CHLORIDE, FLUORIDE AND SULFATE EMISSIONS
Test Run No. 169-3, Location No. 31

	In Coal g %		In Bottom Ash g %		In Collector Ash g %		Stack Gas		Total Recovered g %	
							Particulate g %	Vapor g %		
Chlorine	8645	100	287	3	360	4	insufficient sample	1608 19	2255	26
Fluorine	864	100	12	1	10	1	insufficient sample	77 9	99	11
Sulfate*	67379	100	2373	4	3336	5	492 1	203283 302	209484	311

*Sulfate in coal, ash and particulate is water soluble sulfate as SO_4 .
Sulfate in stack gas vapor includes all sulfur compounds as SO_4 .

TABLE 7-2. ORGANICS EMISSIONS
Test Run No. 169-3, Location No. 31

No.	POM Name	In Coal g %		In Bottom Ash g %		In Collector Ash g %		Stack Gas	
								Particulate g %	Vapor g %
1.	7,12 Dimethylbenz(a)anthracene	none		none		none		insufficient sample	none detected
2.	Benzo(a)pyrene	none		none		0.192 -		insufficient sample	none detected
3.	3 Methylcholanthrene	8.90	100	0.148	2	0.192 2		insufficient sample	none detected
4.	Dibenz(a,h)anthracene	12.71	100	none		none		insufficient sample	none detected

The sulfates were also heavily concentrated in the vapor form and passed through the boiler. In this case, however, the train reagents were able to scrub out the vapors and the sulfate catch in the train was very large indeed. Three times more sulfates were collected than were in the coal. This increase probably was due to the combining of the sulfur and alkali metals in the coal and their being scrubbed out in the bubblers as a sulfate along with the sulfuric acid from the sulfur trioxide.

Two species of polycyclic organic material (POM) were found in the coal. POM 2, benzo[a]pyrene was found only in the dust collector ash and appears to have been a product of the combustion process. This POM had been found in the coal and the hopper ashes in Test 166. The emission of these organics is tabulated in Table 7-2.

The table indicates that POM's were not detected in the stack gas. Since the melting and/or subliming point of these organics is about 475 K or about 50 K above the stack gas temperature, these POM's would be expected to condense on the solid particulate and would not be present in the gas phase. Unfortunately, there was an insufficient sample of stack gas particulate to determine if POM's were deposited on the particulate.

7.2 BOILER AND FUEL CHARACTERISTICS

Boiler number 6 at Location 31 was an Erie City Iron Works brand water tube boiler with four Combustion Engineering gas and coal type RO burners installed in 1963. The pulverized coal burners consisted of a centrally located coal nozzle tip with internal rifling to impart swirl to the coal and air mixture. The combustion air entered the burner throat through circumferentially located vanes which provided swirl to the combustion air. The superheated steam boiler operated at a nominal pressure of 6.31 MPa (900 psig) and temperature

at 756 K (900°F). The nominally balanced-draft furnace operated at -75 Pa (-0.3 inches of water gauge) and had tangent tube wall construction. The combustion air was preheated to approximately 530 K (500°F) with a tubular air preheater.

The tests were run at a boiler load of 148 GJ/hr (140,000 lb/hr) of equivalent saturated steam flow with normal boiler control settings for that load.

This location was a good one for conducting trace species emission testing because it was possible to collect samples both before and after the dust collector. The dust collector was a mechanical cyclone type. A disadvantage was that it proved to be impractical to measure that rate at which ash was deposited in the furnace bottom or the dust collector. It was not possible in actual practice to operate the ash collection system in a way that the amount of ash accumulated over a specific period of time from a particular batch of coal could be determined.

The characteristics of the test boiler and the ashes during the three tests are listed in Table 7-3. The fixed carbon content of the ashes could not be determined because of the high iron content of the samples. With those samples containing large amounts of iron, the sample gained weight during the analysis, making a fixed carbon determination impossible.

The measured total nitrogen oxides emissions from the boiler during the December 1974 combustion modification testing sequence were found to be unusually high, i.e., 562 ng/J (922 ppm, dry at 3% O₂) at an excess oxygen level of 7.4%.⁽⁸⁾ The average emissions from all coal-fired boilers were 290 ng/J at an excess oxygen level of 8.7%. The emissions were rechecked in May 1975 during the trace species testing and again were high at 534 ng/J (874 ppm, dry at 3% O₂) with an excess oxygen level of 7.0%.

TABLE 7-3. BOILER, COAL AND ASH CHARACTERISTICS
Test 169, Location No. 31

Test No.	169-1	169-2	169-3
Date, 1975	April 18	April 18	April 19
Fuel Type	Pulv. Coal	Pulv. Coal	Pulv. Coal
Test Load GJ/hr (10^3 lb/hr)	148 (140)	148 (140)	148 (140)
Excess Oxygen, %	7.0	7.0	7.0
Coal Burned kg (lb)	15586 (34362)	8959 (19750)	10311 (22733)
Coal Proximate Analysis			
AS RECEIVED:			
Moisture, %	7.39	7.65	6.85
Ash, %	10.79	10.18	10.78
Volatile Matter, %	38.75	38.59	38.26
Fixed Carbon, %	43.07	43.58	44.11
Sulfur, %	1.15	1.03	1.28
Heat of Combustion, J/g (Btu/lb)	25,281 (10,871)	25,550 (10,987)	25,897 (11,136)
DRY BASIS:			
Ash, %	11.65	11.02	11.57
Volatile Matter, %	41.84	41.79	41.07
Fixed Carbon, %	46.51	47.19	47.36
Sulfur, %	1.24	1.12	1.37
Heat of Combustion, J/g (Btu/lb)	27,297 (11,738)	27,666 (11,897)	27,801 (11,955)
Bottom and Collector Ash Proximate Analysis			
Moisture, %	1.43	1.56	1.42
Ash, %	96.76	95.99	92.44
Volatiles, %	3.65	4.44	6.11
Fixed Carbon, %	(1)	(1)	0.03
Sulfur, %	0.47	0.55	0.56
Heat of Combustion, %	(1)	(1)	(1)
Fly Ash Proximate Analysis			
Moisture, %	0.08	0.08	0.06
Ash, %	98.68	98.86	99.14
Volatiles, %	1.79	1.45	2.03
Fixed Carbon, %	(1)	(1)	(1)
Sulfur, %	0.29	0.27	0.22
Heat of Combustion, %	239	227	82

(1) Could not be determined due to high iron content of sample

6001-48

The gaseous pollutant emissions during the trace species Test 169-1 are summarized below:

Pollutant	Emissions
Total nitrogen oxides, ng/J (ppm)	561 (918)
Carbon dioxide, %	8.2 (estimated)
Carbon monoxide, ng/J (ppm)	0
Total particulate before dust collector, ng/J (lb/MBtu)	3,016 (7.014)
Total particulate after dust collector, ng/J (lb/MBtu)	1,068 (2.482)

The particulate emissions from this boiler are relatively high. Figure 7-2 from the final report of the combustion modification results⁽⁸⁾ shows the emissions of solid particulate from all coal fuel tests run during the industrial boiler program, and the emission during Test 169 was one of the highest levels measured.

7.3 COLLECTION TRAIN

The trace species sample collection train that was used for test series 169 is pictured and described in Section 3.0.

The contents of the eight bubblers were as follows:

Bubbler No. 1	2% sodium carbonate in water
Bubbler No. 2	2% sodium carbonate in water
Bubbler No. 3	dry
Middle filter	Tenax
Bubbler No. 4	10% HNO_3 + H_2O_2 + AgNO_3 in water
Bubbler No. 5	10% HNO_3 + H_2O_2 + AgNO_3 in water
Bubbler No. 6	10% HNO_3 + H_2O_2 + AgNO_3 in water
Bubbler No. 7	dry
Bubbler No. 8	silica gel

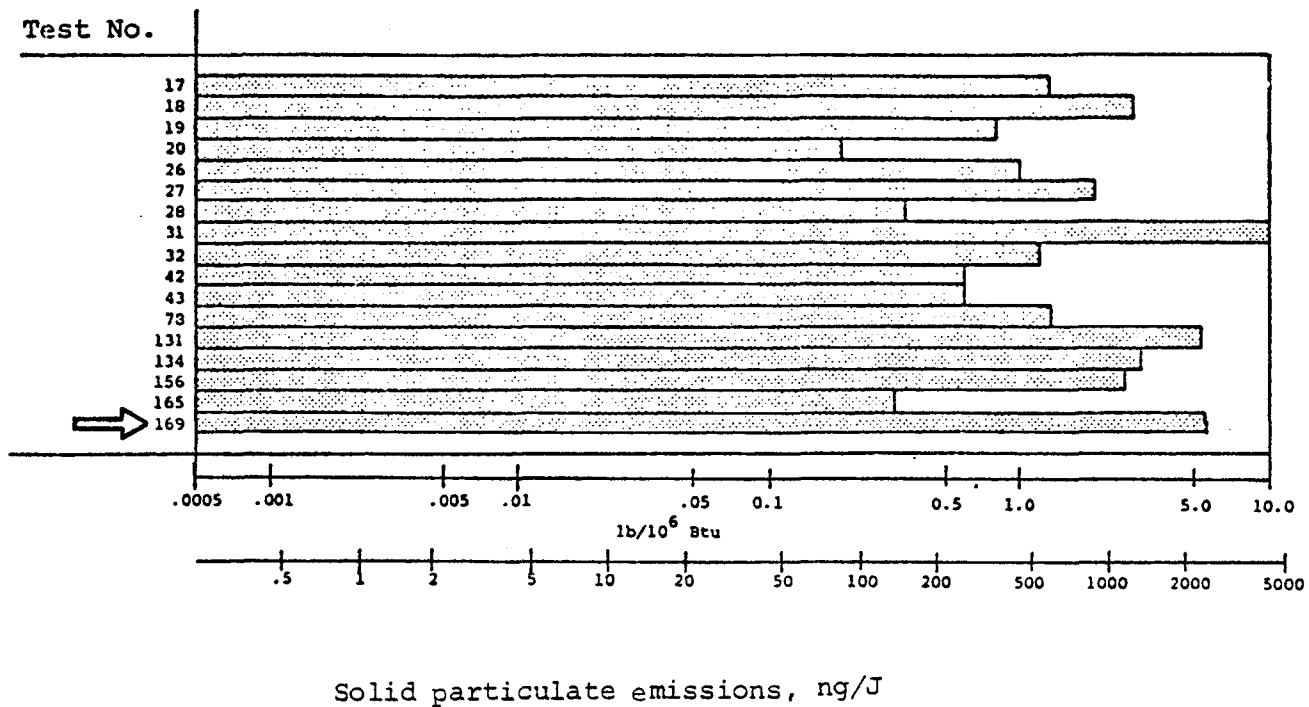


Figure 7-2. Solid particulate emissions at baseload, coal fuel. (8)

The train characteristics for each of the three runs of Test 169 are listed below:

Test Run No.	169-3
Train Operation Duration, min	
Upstream of Collector	103
Downstream of Collector	73
Actual flow volume through train m ³ (ft ³)	
Upstream of Collector	1.70 (60)
Downstream of Collector	0.991 (35)

7.4 SPECIES CONCENTRATIONS

The concentrations of the various species throughout the boiler are listed in Tables 7-4 through 7-6. The concentration of antimony could not be determined because of a chemical interference. The second part of each table lists the mass of the more volatile species, the organics and the sulfates that were scrubbed out of the flue gas stream by the bubblers and the Tenax adsorbent in the trace species train. The bubbler reagents were analyzed only for the more volatile species and the organics.

TABLE 7-4. SPECIES CONCENTRATIONS
Test Run No. 169-1, Location No. 31
Coal Fuel and Ashes

Species	Location of Toxic Material				
	Coal Fuel (µg/g)	Bottom Ash (µg/g)	Collector Ash (µg/g)	Flue Gas Collector Inlet (µg/g)	Flue Gas Collector Outlet (µg/g)
Antimony	Could not be analyzed - chemical interference				
Arsenic	<0.5	2.8	1.2	2.0	4.5
Barium	230	1,300	1,700	3,900	4,100
Beryllium	0.7	0.3	0.21	0.26	0.35
Cadmium	0.6	1.3	0.6	1.4	2.5
Calcium	6,900	77,000	80,000	82,000	82,000
Chromium	14	69	97	109	106
Cobalt	1.5	3	3	2.3	3.1
Copper	26	113	81	95	146
Iron	7,400	85,000	67,000	74,000	61,000
Lead	8.1	45	27	47	56
Manganese	57	480	460	490	450
Mercury	<0.3	0.4	0.4	0.3	0.4
Nickel	<58	80	<56	73	86
Selenium	2.1	7.6	1.7	3.3	16.6
Tin	0.7	3.0	1.0	3.1	2.1
Titanium	720	8,200	9,300	8,500	8,800
Vanadium	79	240	370	520	600
Zinc	16	145	66	144	257
Chloride	580	580	560	*	*
Fluoride	61	30	24	*	*
POM 1†	†	†	†	*	*
POM 2†	†	0.3	0.3	*	*
POM 3†	0.6	†	0.3	*	*
POM 4†	1.2	†	†	*	*
Sulfate #	3100	4900	4300	5000	600

* Insufficient sample for analysis

† None detected

‡ POM 1: 7,12 Dimethylbenz[a]anthracene; POM 2: Benz[a]pyrene; POM 3: 3 Methylcholanthrene;
POM 4: Dibenzo[a,h]anthracene

§ Not analyzed for

Water soluble sulfate.

Continued

6001-48

TABLE 7-4. (Continued)
 Test Run No. 169-1
 Flue Gas Vapor at Dust Collector Inlet

Species	Bubbler Number					
	1 Na ₂ CO ₃ (µg) ³	2 Na ₂ CO ₃ (µg) ³	Tenax (µg)	4 H ₂ O ₂ (µg) ²	5 H ₂ O ₂ (µg) ²	6 H ₂ O ₂ (µg) ²
Antimony	15.8	3.7	§	1.0	1.3	2.0
Arsenic	1.9	2.4	§	8.7	9.1	11.8
Mercury	2.3	<0.2	§			
Selenium	7.6	0.8	§	1.3	1.2	1.3
Chloride	20,000	700	§	§	§	§
Fluoride	12,000	320	§	§	§	§
POM 1†	†	†	360	§	§	§
POM 2†	†	†	†	§	§	§
POM 3†	0.003	†	†	§	§	§
POM 4†	†	†	†	§	§	§
Sulfate #	1.9x10 ⁶	1.6x10 ⁶	§	§	§	§

Flue Gas Vapor At Dust Collector Outlet

Species	Bubbler Number					
	1 Na ₂ CO ₃ (µg) ³	2 Na ₂ CO ₃ (µg) ³	Tenax (µg)	4 H ₂ O ₂ (µg) ²	5 H ₂ O ₂ (µg) ²	6 H ₂ O ₂ (µg) ²
Antimony	12.7	3.7	§	Sample Missing	1.6	1.4
Arsenic	1.6	0.5	§		14.9	6.2
Mercury	5.2	<0.2	§			
Selenium	14.3	0.8	§		0.6	0.7
Chloride	15,000	100	§		<0.4	<0.4
Fluoride	7,400	280	§		§	§
POM 1†	†	†	†		§	§
POM 2†	†	†	0.002		§	§
POM 3†	0.002	†	†		§	§
POM 4†	†	†	†		§	§
Sulfate #	2.1x10 ⁶	0.2x10 ⁶	§		§	§

** Insufficient sample for analysis

† None detected

‡ POM 1: 7,12 Dimethylbenz[a]anthracene; POM 2: Benzo[a]pyrene; POM 3: 3 Methylcholanthrene; POM 4: Dibenz[a,h]anthracene

§ Not analyzed for

Sulfate includes all sulfur compounds expressed as SO₄.

TABLE 7-5. SPECIES CONCENTRATIONS
Test Run No. 169-2, Location No. 31
Coal Fuel and Ashes

Species	Location of Trace Material				
	Coal Fuel (µg/g)	Bottom Ash (µg/g)	Collector Ash (µg/g)	Flue Gas Collector Inlet (µg/g)	Flue Gas Collector Outlet (µg/g)
Antimony	Could not be analyzed - chemical interference				
Arsenic	0.95	0.7	1.0	<0.5	2.5
Barium	330	1,600	1,900	1,400	3,300
Beryllium	0.67	0.3	0.22	0.33	0.62
Cadmium	0.9	1.4	0.5	1.8	4.4
Calcium	10,000	75,000	83,000	80,000	93,000
Chromium	12	92	98	97	149
Cobalt	1.0	3.5	3.0	3.2	7.1
Copper	15	82	81	95	199
Iron	7,900	61,000	71,000	60,000	61,000
Lead	5.3	31	140	121	71
Manganese	67	340	570	370	550
Mercury	<0.3	<0.7	0.6	<0.7	<0.8
Nickel	<61	55	<61	<61	<149
Selenium	2.5	12	1.5	1.4	9.9
Tin	0.7	3.5	1.6	2.1	5.2
Titanium	800	8,100	9,400	9,500	8,600
Vanadium	63	230	370	350	400
Zinc	19	132	67	89	224
Chloride	600	590	520	*	*
Fluoride	60	21	69	• *	*
POM 1 ‡	†	†	†	*	*
POM 2 ‡	†	0.3	†	*	*
POM 3 ‡	0.5	0.3	0.3	*	*
POM 4 ‡	†	†	†	*	*
Sulfate #	5,500	4,900	6,300	7,000	200

* Insufficient sample for analysis

† None detected

‡ POM 1: 7,12 Dimethylbenz[a]anthracene; POM 2: Benzo[a]pyrene; POM 3: 3 Methylcholanthrene;
POM 4: Dibenz[a,h]anthracene

Water soluble sulfate.

Continued

6001-48

Table 7-5. Continued
Test Run No. 169-2

Flue Gas Vapor At Dust Collector Inlet

Species	Bubbler Number					
	1 Na ₂ CO ₃ (µg)	2 Na ₂ CO ₃ (µg)	Tenax (µg)	4 H ₂ O ₂ (µg)	5 H ₂ O ₂ (µg)	6 H ₂ O ₂ (µg)
Antimony	<0.05	<0.05	§	1.5	0.5	0.2
Arsenic	0.8	<0.06	§	4.2	4.5	3.3
Mercury	0.3	<0.1	§	<0.4	<0.4	<0.4
Selenium	40	0.9	§	<1.0	<1.0	<1.0
Chloride	5,300	100	§	§	§	§
Fluoride	1,100	340	§	§	§	§
POM 1 ‡	†	†	†	§	§	§
POM 2 ‡	†	†	†	§	§	§
POM 3 ‡	0.048	0.032	†	§	§	§
POM 4 ‡	0.002	†	†	§	§	§
Sulfate #	4.1x10 ⁶	0.7x10 ⁶	§	§	§	§

Flue Gas Vapor At Dust Collector Outlet

Species	Bubbler Number					
	1 Na ₂ CO ₃ (µg)	2 Na ₂ CO ₃ (µg)	Tenax (µg)	4 H ₂ O ₂ (µg)	5 H ₂ O ₂ (µg)	6 H ₂ O ₂ (µg)
Antimony	0.14	0.16	§	1.5	0.5	0.2
Arsenic	0.7	0.5	§	5.3	4.8	0.1
Mercury	0.3	0.8	§	<0.4	<0.4	<0.4
Selenium	11.6	1.0	§	<1.0	<1.0	<1.0
Chloride	1,600	100	§	§	§	§
Fluoride	3,700	250	§	§	§	§
POM 1 ‡	†	†	†	§	§	§
POM 2 ‡	0.002	†	0.002	§	§	§
POM 3 ‡	0.30	†	†	§	§	§
POM 4 ‡	†	†	†	§	§	§
Sulfate #	2.4x10 ⁶	0.1x10 ⁶	§	§	§	§

* Insufficient sample for analysis

† None detected

‡ POM 1: 7,12 Dimethylbenz[a]anthracene; POM 2: Benzo[a]pyrene; POM 3: 3 Methylcholanthrene; POM 4: Dibenz[a,h]anthracene

§ Not analyzed for

Sulfate includes all sulfur compounds expressed as SO₄.

6001-48

TABLE 7-6. SPECIES CONCENTRATIONS
Test Run No. 169-3, Location No. 31
Coal Fuel and Ashes

Species	Location of Trace Material				
	Coal Fuel (µg/g)	Bottom Ash (µg/g)	Collector Ash (µg/g)	Flue Gas Collector Inlet (µg/g)	Flue Gas Collector Outlet (µg/g)
Antimony	Could not be analyzed - chemical interference				
Arsenic	3	0.5	0.5	3.2	3.1
Barium	210	1,200	1,900	1,300	1,000
Beryllium	1.8	0.27	0.31	0.35	0.73
Cadmium	0.6	0.9	0.6	1.0	1.6
Calcium	9,000	68,000	87,000	78,000	77,000
Chromium	22	88	98	106	120
Cobalt	1.6	3.2	2.8	2.7	3.7
Copper	30	90	78	103	151
Iron	10,000	69,000	72,000	83,000	61,000
Lead	22	48	31	47	44
Manganese	70	450	520	490	390
Mercury	<0.3	0.5	0.6	<0.6	<0.7
Nickel	<60	62	63	79	104
Selenium	6.6	<1.0	<1.0	2.3	14
Tin	0.6	1.6	1.5	1.0	2.6
Titanium	740	8,400	8,900	8,100	8,100
Vanadium	44	220	370	300	410
Zinc	35	130	73	150	203
Chloride	680	580	560	*	*
Fluoride	68	24	15	*	*
POM 1†	†	†	†	*	*
POM 2‡	†	†	0.3	*	*
POM 3‡	0.7	0.3	0.3	*	*
POM 4‡	1.0	†	†	*	*
Sulfate#	5,300	4,800	5,200	4,700	1,400

* Insufficient sample for analysis

† None detected

‡ POM 1: 7,12 Dimethylbenz[a]anthracene; POM 2: Benzo[a]pyrene; POM 3: 3 Methylcholanthrene;
POM 4: Dibenzo[a,h]anthracene

Water soluble sulfate.

Continued

TABLE 7-6. (Continued)
Test Run No. 169-3
Flue Gas Vapor At Dust Collector Inlet

Species	Bubbler Number					
	1 Na ₂ CO ₃ (µg)	2 Na ₂ CO ₃ (µg)	Tenax (µg)	4 H ₂ O ₂ (µg)	5 H ₂ O ₂ (µg)	6 H ₂ O ₂ (µg)
Antimony	0.10	0.12	§	<0.2	<0.2	<0.2
Arsenic	22.3	4.4	§	0.01	3.8	3.9
Mercury	0.03	0.01	§	<0.04	<0.04	<0.04
Selenium	9.1	0.6	§	<1.0	<1.0	<1.0
Chloride	64,000	400	§	§	§	§
Fluoride	6,900	600	§	§	§	§
POM 1 ‡	†	†	†	§	§	§
POM 2 ‡	†	†	†	§	§	§
POM 3 ‡	†	†	†	§	§	§
POM 4 ‡	†	†	†	§	§	§
Sulfate #	0.8x10 ⁶	0.3x10 ⁶	§	§	§	§

Flue Gas Vapor At Dust Collector Outlet

Species	Bubbler Number					
	1 Na ₂ CO ₃ (µg)	2 Na ₂ CO ₃ (µg)	Tenax (µg)	4 H ₂ O ₂ (µg)	5 H ₂ O ₂ (µg)	6 H ₂ O ₂ (µg)
Antimony	0.14	0.22	§	<0.2	<0.2	<0.2
Arsenic	8.9	3.7	§	0.01	5.5	5.6
Mercury	0.01	0.19	§	<0.04	<0.04	<0.04
Selenium	10.2	0.5	§	<1.0	<1.0	<1.0
Chloride	18,000	200	§	§	§	§
Fluoride	580	290	§	§	§	§
POM 1 ‡	†	†	†	§	§	§
POM 2 ‡	†	†	†	§	§	§
POM 3 ‡	†	†	†	§	§	§
POM 4 ‡	†	†	†	§	§	§
Sulfate #	2.1x10 ⁶	0.2x10 ⁶	§	§	§	§

* Insufficient sample for analysis

† None detected

‡ POM 1: 7,12 Dimethylbenz[a]anthracene; POM 2: Benzo[a]pyrene;
POM 3: 3 Methylcholanthrene; POM 4: Dibenz[a,h]anthracene

§ Not analyzed for

Sulfate includes all sulfur compounds expressed as SO₄.

6001-48

SECTION 8.0

SPECIAL REAGENT COMPARISON TEST

The reagents that had been used at Location 31 and 35 were erratic in their ability to scrub out the volatile elements from the flue gas. Consequently, a special test was designed where three sample collection trains containing different sets of reagents that had been developed for the EPA by three different laboratories were used simultaneously by KVB to collect trace elements from the same boiler. The objective was to use one coal having a known trace element content in a boiler where all of the ashes could be collected and weighed individually. It then would be possible to compare directly the collection efficiency of each of the three reagent sets.

8.1 SAMPLE COLLECTION EQUIPMENT

The comparison test was set up in the combustion research laboratory of KVB, Inc. using an eighty horsepower Ben B. Hood brand fire-tube boiler. The salient advantage of this particular boiler was that all of the ashes generated by a test could be identified and collected. Prior to a test, the furnace tube, firetubes and flues were cleaned out. After a test they were cleaned out again and all of the ashes collected for weighing and analysis. The Foster Wheeler Company burner had been modified so measured amounts of pulverized coal could be fed from the hopper. The burner design was such that liquid fuel additives could be injected into the primary air just upstream of the ignition point. This test site was assigned the test location number 40.

The boiler, its flues and the location of the sampling ports are shown schematically in Figure 8-1. The four sampling ports are located in the vertical flue section on the right where the flue gas flow is downward.

One of the three collection trains had been developed by the Midwest Research Laboratories in Kansas City, Missouri. This train consisted of a cyclone, a glass-fiber filter, an adsorber filter and eight bubblers in series. The contents of the bubblers are listed on the schematic drawings of Train "M" that is shown in Figure 8-2. This train was used by KVB, Inc. for all of the previous trace species testing in the field and is discussed in detail in Section 3.0.

Train M was used in its complete form which included the Tenax adsorbent that was intended primarily for the removal of organic materials, i.e., POM. The other two trains were intended to remove only trace elements from the flue gas stream, since it was not the purpose of this particular test to collect and analyze organic material.

The second train was designated Train T and it was basically an Aerotherm Acurex Corporation High Volume Stack Sampler with reagents that had been developed by TRW Systems, Inc. in the four impingers.^(30,31) The contents of the impingers are listed in Figure 8-2.

The third train was developed by R. M. Statnick, et al of the Process Measurements Branch, Industrial Environmental Research Laboratory of the U.S. Environmental Protection Agency at Research Triangle Park, NC.⁽⁴¹⁾ It is also shown schematically in Figure 8-2. This train was designated Train S and the bubbler reagents are listed under Train S in Figure 8-2.

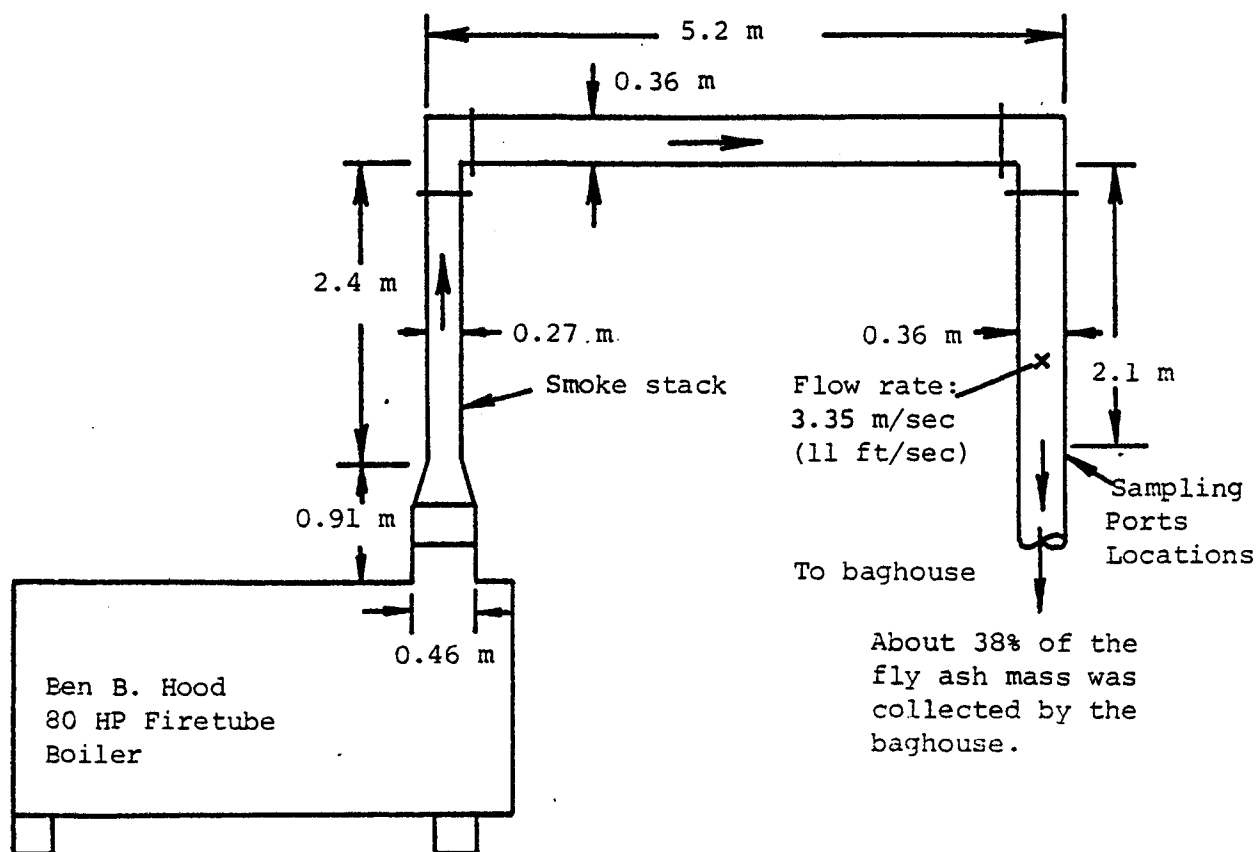


Figure 8-1. Test boiler installation.

6001-48

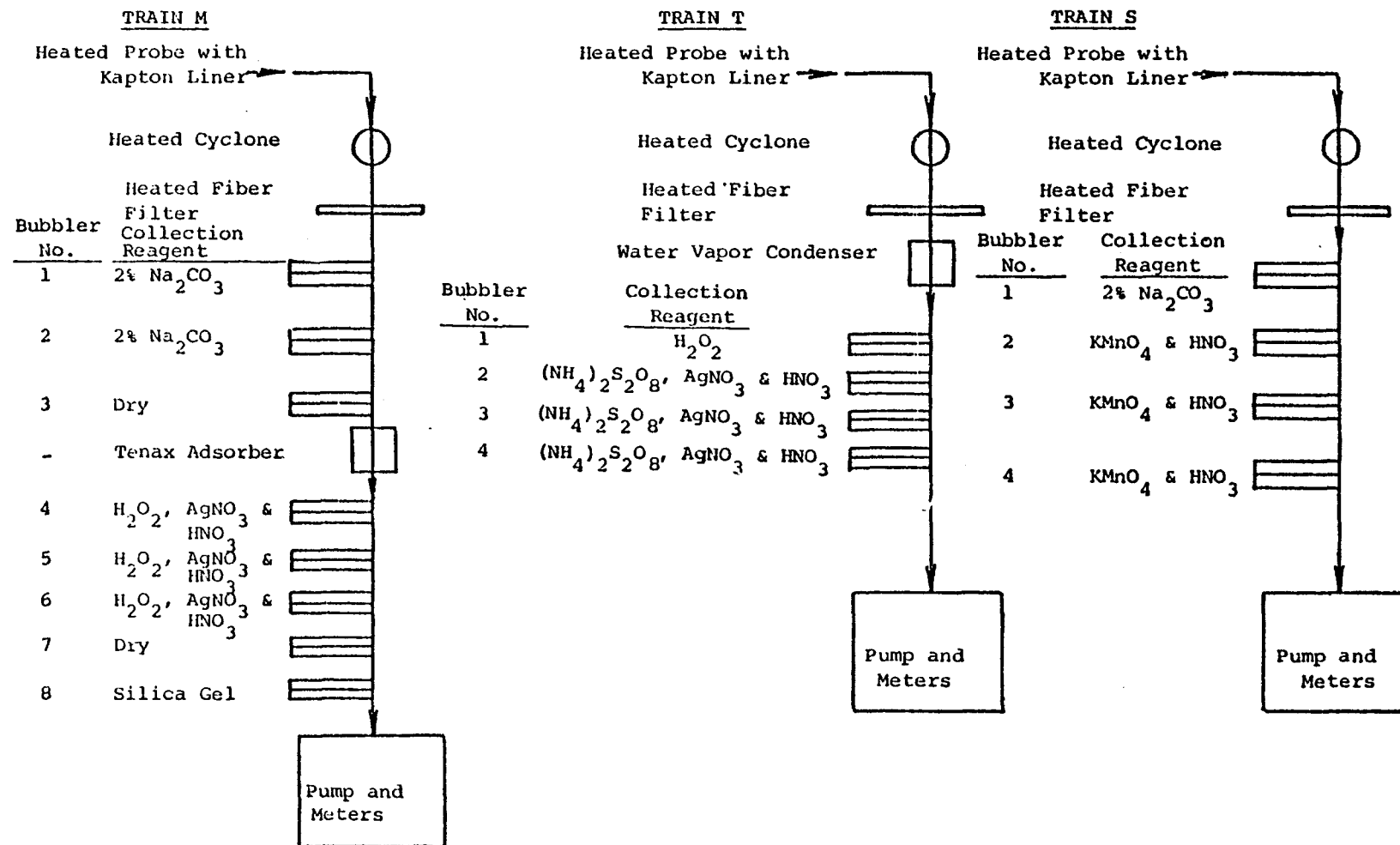


Figure 8-2. Sampling train schematics.

The Train S design was developed specifically for the collection of mercury vapor from a flue gas stream that contains a high concentration of sulfur dioxide. In order to make the sampling procedure for mercury compatible with streams containing 0.1 to 8% v/v of sulfur dioxide, a prescrubber was used to selectively and quantitatively remove all of the sulfur dioxide present. Experience had shown various alkaline scrubbing media to be effective for sulfur dioxide removal, and so a prescrubber containing saturated sodium carbonate solution was employed in bubbler no. 1. The nitric acid-potassium permanganate reagent was selected for the other three bubblers because of ease of preparation in the field and the general availability of reagents.

The coal burned for the test was especially selected for its mercury content of from 0.10 to 0.28 $\mu\text{g/g}$. The Peabody Coal Company office in St. Louis, Missouri made available to the program about 2,000 kg (2 tons) of unwashed coal from their Kentucky No. 9 mine.

In order to assure a high level of mercury in the boiler feed, the coal also was "doped" with an aqueous solution of mercuric chloride having a strength equivalent to 0.1 microgram of mercury per gram of coal burned. Four liters of a solution were prepared that contained 0.1263 g of mercuric chloride in distilled water. A measured amount of this solution was sprayed under nitrogen pressure into the primary air of the pulverized coal burner during both test runs.

8.2 ANALYTICAL METHODS AND DATA

Analytical methods: Seven types of solid samples were analyzed for their trace element content by the Midwest Research Institute of Kansas City, MO. The seven solids were: coal, furnace tube ash, firetube ash, lower stack ash, duct ash, baghouse ash, and the particulate catch from the three mass sampling trains. The solid samples were prepared for analysis by digesting 0.5 g of solid with 3 ml hydrofluoric acid and 1 ml nitric acid in a Parr bomb at 130°C for 18 hours. Boric acid was added (1.5 g) and diluted to 25 ml.

A portion of each impinger solution was heated with permanganate and nitric acid prior to analysis for mercury and selenium. Sulfuric acid was added to another portion of each impinger solution and heated with a reflux condenser before analysis for arsenic and antimony.

Acid oxidizing impingers were analyzed directly for ten other elements: beryllium, cadmium, chromium, copper, lead, manganese, nickel, silver, titanium, and zinc. A portion of the sodium carbonate impingers were acidified before analysis for these others.

Mercury was analyzed by the cold vapor technique. Antimony, arsenic, and selenium were analyzed by atomic absorption following addition of sodium borohydride. The volatile hydrides that were formed were swept into a nitrogen-entrained air-hydrogen flame and analyzed. The ten additional elements were analyzed by conventional flame-atomization atomic-absorption procedures.

Data: A summary of the boiler operational data for Tests 213 and 214 is given in Table 8-1. This table indicates the amounts of coal burned and the ashes collected. The operational data for each sampling train are presented in Table 8-2.

The trace element concentrations of the coal and ashes determined by MRI are listed in Table 8-3. The trace element content of the particulate collected by the probe liner, cyclone and filter, by the bubblers and by the Tenax adsorber are listed in Tables 8-4, 8-5, and 8-6. The data shown in Tables 8-3 through 8-6 were taken from Reference 40.

8.3 RESULTS

A number of difficulties were experienced in conducting these laboratory tests to the extent that the precision obtained was less than was desired. For that reason, the results in Table 8-4, 8-5, and 8-6 should be used only for qualitative rather than quantitative comparisons. The trace element analyses of the coal and ashes is not covered by this comment and the data in Table 8-3 are accurate and useful in evaluating relative concentrations in the ash.

TABLE 8-1. TEST BOILER AND FUEL DATA SUMMARY

Location 40

Test No.	213	214
Date, 1975	August 25	August 28
Fuel Type	Pulver. Coal	Pulver. Coal
Burner Type	Pulverizer	Pulverizer
Test Load, GJ/hr (10^3 lb/hr)	2.19 (2.08)	2.15 (2.04)
Excess Oxygen, %	7.2	7.4
Boiler Operation, min	129	153
Coal Burned, kg (lb)	156 (344)	192 (425)
Coal Doping with Mercury		
Amount HgCl solution used, g	1009.7	787.7
Amount Hg injected, g	0.02310	0.01837
Mercury concentration in coal, $\mu\text{g}/\text{min}$	169	163
Mercury concentration injected, $\mu\text{g}/\text{min}$	289	353
Effective total Hg concentration in coal, $\mu\text{g}/\text{min}$	458	516
Boiler Operation, min	129	153
Coal Burned, kg (lb)	156 (344)	192 (425)
Ash Collected, kg (lb)		
Furnace tube	4.535 (10.0)	5.443 (12.0)
Firetubes	6.123 (13.5)	6.350 (14.0)
Breeching	0.2211 (0.487)	0.2935 (0.647)
Stack and flue	0.0981 (0.216)	0.4733 (1.04)
Bag house	8.618 (19.0)	7.484 (16.5)
Total Ash Collected	19.59 (43.20)	20.04 (44.19)
Stack Gas Speed, m/sec (ft/sec)	3.35 (11.0)	
Stack Gas Flow Rate, $\text{std m}^3/\text{sec}$ ($\text{std ft}^3/\text{sec}$)	.193 (6.86)	
Stack Gas Temperature, K ($^{\circ}\text{F}$)	454 (355)	

6001-48

TABLE 8-2. TRACE SPECIES TRAIN CHARACTERISTICS
Location 40

Test No.	213	214
Test Duration, min		
Train M	88	93
Train T	78	47
Train S	88	87
Actual flow rate through train, m ³ /min (ft ³ /min)		
Train M	0.01636 (0.578)	0.01827 (0.645)
Train T	0.03610 (1.275)	0.03653 (1.29)
Train S	0.02070 (0.7312)	0.02113 (0.6942)
Actual volume through train, m ³ (ft ³)		
Train M	1.440 (50.86)	1.699 (60.0)
Train T	2.816 (99.47)	1.710 (60.4)
Train S	1.822 (64.35)	1.710 (60.4)
Particulate collected by probe, cyclone and filter, g (lb)		
Train M	1.810 (0.00398)	1.040 (0.00229)
Train T	4.652 (0.01023)	2.658 (0.00584)
Train S	1.302 (0.00286)	1.098 (0.00242)

6001-48

TABLE 8-3. TRACE ELEMENT CONTENT OF COAL AND ASHES

Element	Test No.	Coal (µg/g)	Furnace Ash (µg/g)	Firetube Ash (µg/g)	Lower Stack Ash (µg/g)	Duct Ash (µg/g)	Baghouse Ash (µg/g)
Antimony	213	<4 (3.9)†	<2	<2	<2	<2	<2
	214	<4 (3.9)†	<2	<2	<2	<2	*
Arsenic	213	<10 (14) †	<2	7	18	<2	<2
	214	<10 (14) †	<2	6	15	<2	*
Beryllium	213	1.2	9.8	7.9	6.4	12	9.5
	214	1.4	12.5	9.8	8.6	11.5	*
Cadmium	213	<3 (0.9)†	<4	<4	5.2	<4	<4
	214	<3 (0.9)†	<4	<4	7.1	<4	*
Chromium	213	36	1,140	130	307	66	171
	214	44	1,180	126	272	154	*
Copper	213	14	118	125	162	116	137
	214	15	164	87	113	97	*
Lead	213	<20 (11) †	30	65	110	65	100
	214	<22 (11) †	27	39	74	61	*
Manganese	213	37	319	408	690	545	350
	214	34	640	127	340	305	*
Mercury	213	0.14(.11-.28)†	0.3	1.7	2.8	2.3	2.7
	214	0.13(.11-.28)†	1.2	2.3	3.7	1.5	*
Nickel	213	21	610	78	150	26	90
	214	24	585	51	96	60	*
Selenium	213	<5 (2.6)†	4.1	19	52	32	16
	214	1.7	<5	20	35	22	*
Silver	213	<4 (0.06)†	1.8	<0.1	3.0	<0.1	0.1
	214	<4 (0.06)†	1.1	<0.1	0.3	0.2	*
Titanium	213	650	5,900	5,200	4,400	7,400	4,600
	214	630	6,900	4,400	4,200	6,900	*
Zinc	213	24	182	136	2,200	3,500	130
	214	22	190	140	700	1,400	*

* Sample was lost; only total weight was recorded.

† Kentucky coal analysis by Illinois Geological Survey.

6001-48

TABLE 8-4. TRACE ELEMENT ANALYSIS OF TRAIN M

Element	Test No.	Particulate ($\mu\text{g/g}$)	Bubbler 1 Na_2CO_3 (μg)	Bubbler 2 Na_2CO_3 (μg)	Tenax (μg)	Bubbler 4 H_2O_2 (μg)	Bubbler 5 H_2O_2 (μg)	Bubbler 6 H_2O_2 (μg)
Antimony	213	<5	0.13	<0.1	<0.5	<7	<7	<7
	214	<5	0.77	<0.1	<0.5	<7	<7	<7
Arsenic	213	<2	<0.5	1.1	<0.8	<0.4	0.8	<0.3
	214	<2	<0.4	0.6	<0.8	<0.3	0.3	1.9
Beryllium	213	20	<8	<8	<2	<6	<6	<6
	214	19	<8	<8	<2	<6	<6	<6
Cadmium	213	<3	<30	<30	<3	<22	<22	<22
	214	<3	<30	<30	<3	<22	<22	<22
Chromium	213	152	<44	<44	<19	<37	<37	<37
	214	88	<44	<44	<17	<37	<37	<37
Copper	213	159	3	126	<25	<12	<12	<12
	214	90	8	38	<25	<12	<12	<12
Lead	213	48	<134	<130	<41	<102	<102	<102
	214	46	<130	<130	<41	<102	<102	<102
Manganese	213	213	7	40	<2	82	<23	<23
	214	176	11	<3	<2	<23	<23	<23
Mercury	213	3.9	1.5	0.5	0.6	<0.01	0.3	<0.01
	214	2.1	0.1	0.3	0.4	0.7	0.3	0.5
Nickel	213	45	<33	<33	<10	<26	<26	<26
	214	37	<33	<33	<10	<24	<26	<26
Selenium	213	6.1	5.2	2.9	<1	*	*	*
	214	6.1	4.5	4.3	<1	*	*	*
Silver	213	<8	<27	<27	<8	†	†	†
	214	<8	<27	<27	<8	†	†	†
Titanium	213	9,700	<120	<120	<40	<100	<100	<100
	214	9,900	<120	<120	<40	<100	<100	<100
Zinc	213	267	60	<30	<15	<30	<30	<30
	214	192	45	<30	<15	<30	<30	<30

* A spike cannot be recovered from this solution.

6001-48

† Impinger solution contains silver nitrate.

TABLE 8-5. TRACE ELEMENT ANALYSIS OF TRAIN T

Element	Test No.	Particulate ($\mu\text{g/g}$)	Condenser (μg)	Bubbler 1 H_2O_2 (μg)	Bubbler 2 $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (μg)	Bubbler 3 $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (μg)
Antimony	213	<4	<6	<10	<12	<12
	214	<4	<3	<10	<12	<12
Arsenic	213	4.0	1.3	0.3	1.1	2.0
	214	3.0	1.2	0.5	1.2	1.2
Beryllium	213	20	<5	<9	<8	<8
	214	23	<2	<9	<8	<8
Cadmium	213	4.0	<19	<33	<40	<40
	214	1.7	<8	<33	<40	<40
Chromium	213	92	828	<56	91	134
	214	129	455	<56	99	97
Copper	213	130	27	<13	<13	<13
	214	124	17	<12	<13	<13
Lead	213	99	131	<160	<140	<140
	214	97	<41	<140	<140	<140
Manganese	213	115	446	<13	<18	<11
	214	214	245	<13	<18	<7
Mercury	213	2.4	0.1	0.9	1.2	0.8
	214	2.6	1.1	1.9	0.9	<0.03
Nickel	213	52	698	<38	<45	<45
	214	44	643	<34	<45	<45
Selenium	213	7.3	<14	<23	*	*
	214	6.3	<14	<23	*	*
Silver	213	19	<18	91	†	†
	214	9	<8	167	†	†
Titanium	213	9,700	<90	<150	<180	<180
	214	13,000	<40	<150	<180	<180
Zinc	213	220	60	45	91	192
	214	230	17	40	89	103

* A spike cannot be recovered from this solution.

† Impinger solution contains silver nitrate.

6001-48

TABLE 8-6. TRACE ELEMENT ANALYSIS OF TRAIN S

Element	Test No.	Particulate ($\mu\text{g/g}$)	Bubbler 1 Na_2CO_3 (μg)	Bubbler 2 KMnO_4 (μg)	Bubbler 3 KMnO_4 (μg)	Bubbler 4 KMnO_4 (μg)	Oxalic Acid Rinse (μg)
Antimony	213	<22	<4	<4	<4	†	<5
	214	*	0.6	<4	<4	<4	<5
Arsenic	213	<11	1.2	0.5	1.3	†	4.6
	214	*	6.0	<4	0.8	1.3	1.7
Beryllium	213	22	<8	<3	<3	†	<6
	214	23	<8	<3	<3	<3	<6
Cadmium	213	<3	<3	<10	<10	†	<18
	214	<3	<3	<10	<10	<10	<18
Chromium	213	123	54	<26	<26	†	<20
	214	138	47	<26	<26	<26	<20
Copper	213	65	<10	<5	<5	†	<17
	214	113	<10	<5	<5	<5	<17
Lead	213	41	<130	<25	<25	†	<80
	214	33	<130	<25	<25	<25	<80
Manganese	213	209	30	‡	‡	‡	‡
	214	216	29	‡	‡	‡	‡
Mercury	213	3.1	3.4	1.2	0.5	†	0.2
	214	3.8	1.3	3.6	1.2	0.8	0.3
Nickel	213	38	<14	<14	<14	†	<20
	214	35	<30	<14	<14	<14	<20
Selenium	213	6.5	4.4	<8	<8	†	<12
	214	6.5	4.6	<8	<8	<8	<12
Silver	213	<4	<20	<16	<16	†	<17
	214	20	<20	<16	<16	<16	<17
Titanium	213	11,000	<125	<23	<23	†	<77
	214	10,000	<110	<23	<23	<23	<77
Zinc	213	241	47	78	47	†	<5
	214	225	35	46	92	67	<5

* Insufficient sample.

† Sample missing.

‡ Impinger solution contains manganese.

6001-48

Unfortunately, the difficulties experienced in the train comparison tests involved both the sampling and the laboratory analysis. The particulate catch and loadings may not have been representative since the trains were not operated isokinetically. The sampling at nearly twice the isokinetic rate may have had some impact on the retention of trace metals by the bubblers. However, since the trains were operated under close to similar conditions and sample times, the data is useful for qualitative comparisons of train performance.

The major limitations in the laboratory analysis concerned the analysis of the coal for mercury and low concentrations of elements in bubbler solutions. The initial analysis of the coal for mercury content indicated a concentration of 2.6 $\mu\text{g/g}$ which is higher than any large coal source in the United States. A very poor material balance resulted from the use of this concentration and a reanalysis of the coal was requested. The final analysis of 0.14 $\mu\text{g/g}$ is more typical of the coal used with a resulting shift from a grossly underbalanced to somewhat overbalanced condition for mercury.

The second limitation in performing a materials balance was the very low concentrations in the bubbler solutions. Although the trains were operated for what were considered to be more than adequate sample times, a large number of elemental analyses proved to be below the detection limits for these species. A reexamination of this situation revealed that this condition would likely have existed even if the sampling had been conducted isokinetically.

Acknowledging the limitations outlined above, the qualitative data comparing the material balances for the three trains are shown in Figure 8-3 and Table 8-7. Comparisons are made only for four of the volatile elements which had been difficult to scrub out of the stack gases. The balances that were achieved with these four are indicative of the balances that could be obtained for the entire list of elements in Tables 8-4, 8-5, and 8-6.

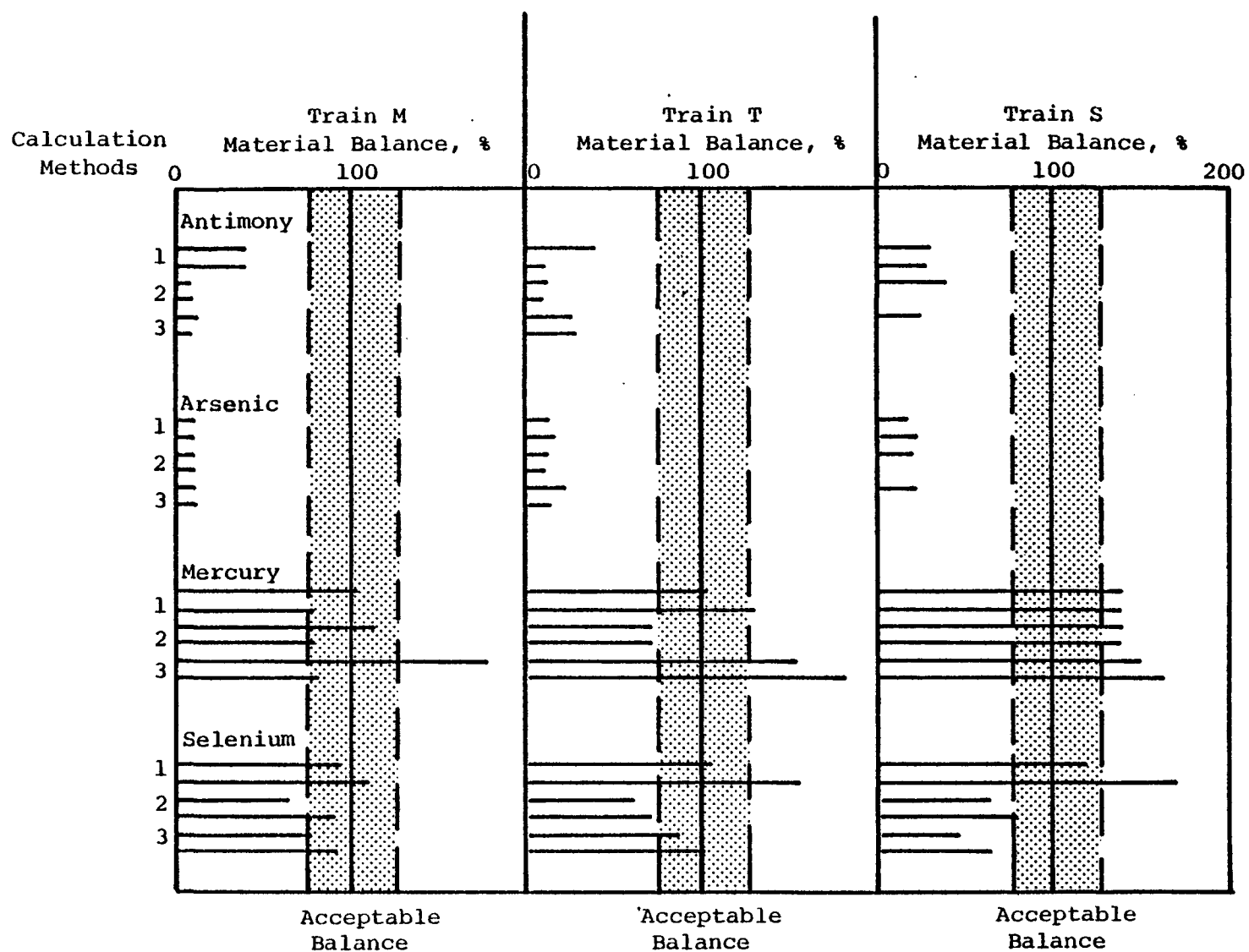


Figure 8-3. Material balances for the three sample collection trains.

TABLE 8-7. MATERIAL BALANCES BY THREE CALCULATION METHODS

Element and Test No.	Train M			Train T			Train S		
	Calc. Method No.			Calc. Method No.			Calc. Method No.		
	1	2	3	1	2	3	1	2	3
	Material Balance			Material Balance			Material Balance		
	% of input			% of input			% of input		
Antimony									
213	39	8	12	40	12	25	31	39	24
214	41	8	10	11	10	29	28	*	*
Arsenic									
213	11	10	10	13	13	22	16	20	20
214	12	10	11	16	10	16	22	*	*
Mercury									
213	107	113	179	105	72	155	138	139	148
214	81	79	81	131	72	183	139	138	162
Selenium									
213	94	64	77	105	60	86	116	63	45
214	112	90	90	157	69	102	170	77	62

* The quantity of the sample was insufficient for analysis.

6001-48

Since it was possible to collect, weigh and analyze for trace element content all of the ashes, as well as the fly ash from the flue gas, three methods of calculating a material balance were used. These were:

1. Baghouse catch was used for the flue gas fly ash content, rather than the particulate collected by the cyclone and front filter as is conventional in an EPA Method 5 analysis.
2. The ratio of the mass of the baghouse catch to the mass of the particulate catch of the train was used to calculate the total grain loading of the entire flue gas stream.
3. The ratio of the total quantity of flue gas to the quantity of flue gas actually sampled by the train was used to calculate the total grain loading of the entire flue gas stream.

Material balances were calculated for each of the three trains using the three calculation methods described above. The balances shown in Figure 8-3 and the percentages of closure listed in Table 8-7 are based on data taken from Reference 40. An entry of 100% indicates that one hundred percent of the element that was input with the coal was recovered in the boiler.

The selenium balanced in about one-half of the calculations. A balance of from 75% to 125% was deemed to be an acceptable balance. The mercury balanced six times out of the eighteen calculations, and five of these were from the Train M data. The antimony and arsenic did not balance in any instance. These metals consistently were very much underbalanced, and it appears that the reagents were incapable of scrubbing out antimony and arsenic vapors from the flue gas.

The mercury balances were about evenly divided between underbalanced and overbalanced with the five successful runs of Train M. With the same train the selenium was predominately underbalanced; however with Trains T and S it was more evenly divided between under- and overbalance. Calculation method 1 produced balances that were predominately above 100%; while methods 2 and 3 produced balances that were usually below 100%.

SECTION 9.0

ELEMENT PARTITIONING AND PARTICULATE ENRICHMENT

Combustion of coal and oil fuels releases the trace elements that are contained in the fuel as vapors and particulates, and certain elements tend to be concentrated in the ash that collects in particular parts of the boiler and/or in fly ash of a particular size. The tendency to concentrate in the waste that collects in certain parts of a boiler commonly is called "element partitioning" and the tendency to concentrate in particulates of a certain size is called "particulate enrichment." Both phenomena were observed during the testing by XVB, Inc.

Workers in the field have observed three classes of partitioning in a coal-fired boiler: (43,44)

Class I: Twenty elements--Al, Ba, Ca, Ce, Co, Eu, Fe, Hf, K, La, Mg, Mn, Rb, Sc, Si, Sm, Sr, Ta, Th, and Ti--tended to be deposited in the bottom ash or slag in a concentration about seven times greater than in the coal fuel. These elements were partitioned about equally between the bottom ash and the collector inlet fly ash. They did not tend to concentrate in a dust collector, and the concentrations in the inlet and outlet fly ashes were about equal.

Class II: Nine elements--As, Cd, Cu, Ga, Pb, Sb, Se, Zn, and Sn--tended not to be incorporated into the bottom ash and the concentration in the bottom ash was about one-third of that in the coal. The concentration in the inlet fly ash was about two times greater than in the coal, and in the outlet fly ash it was about eighteen times greater.

Class III: Hg, Cl, and Br remained essentially completely in the gas phase. (F may behave similarly.)

The other elements--Cr, Cs, Na, Ni, U, and V--could not be definitely assigned to a class based on their data but appeared to be intermediate between Classes I and II.

Volatilization-condensation or adsorption mechanisms have been proposed to rationalize the classes of behavior observed for the various elements.⁽¹²⁾

Class I. These elements are not volatilized in the combustion zone, but instead form a melt of rather uniform composition that becomes both fly ash and slag. The slag is removed directly and quickly from the combustion zone, while the fly ash remains in contact with the cooling flue gas. The Class I elements remain in the condensed state, and hence show little partitioning between slag, inlet fly ash, and outlet fly ash.

Class II. These elements are volatilized on combustion. Since the slag or bottom ash is removed from the combustion zone, they have no opportunity to condense on the slag or ash. They do, however, condense or become adsorbed on the fly ash as the flue gas cools. These elements thus are depleted preferentially from the slag (partitioning effect), and preferentially concentrated on the outlet fly ash compared to the inlet fly ash (particle size effect).

Although most Class II and Class III elements have relatively low boiling points, and most Class I elements have relatively high boiling points, there are enough exceptions to make it unlikely that the elemental boiling point is the major factor determining elemental partitioning. For example, Ca and Cu behave as if they have low boiling points, while Rb, Cs, and Mg behave as if they have high boiling points. It is more probable that the physicochemical properties of the elements and their chemical compounds in the coal and combustion products, the nature of the coal-burning process, and the mechanisms occurring in the control devices all determine the behavior upon combustion. The following six formation mechanisms have been proposed.⁽⁴³⁾

1. Trace elements in coal are present in aluminosilicates, as inorganic sulfides, or as organic complexes.
2. On combustion the aluminosilicates are not decomposed. Rather, they melt and coalesce to form the slag or bottom ash and fly ash.

3. During the initial stages of combustion, the conditions in a coal particle and within its immediate vicinity are probably reducing. Under these conditions the chemical bonding between metallic elements and sulfur in sulfide mineral inclusions or between the elements and the organic matrix is broken, and these elements form volatile species. If the elements are dispersed in the coal organic matrix, they become initially dispersed in the gas stream when the coal is burned. Thus, even those elements that are not as stable as the vapor at the combustion temperature initially enter the flue gas stream as a vapor.
4. The elements initially volatilized or dispersed in the flue gas stream may be oxidized to form less volatile species which then may condense or be adsorbed on the fly ash as the temperature of the flue gas drops.
5. Since the slag is in contact with the flue gas for a short time, and at a high temperature, the condensation of volatiles on the slag is not great.
6. Increasing concentrations of Class II elements in samples collected successively downstream in and near the particulate control devices are a result of the particle-size-dependent collection efficiencies of these devices in which larger particles are more efficiently captured than smaller particles. Thus, the finer particles penetrating the control devices contain higher concentrations of Class II elements than the coarser, collected particles.

Referring to paragraph number 4 above, the metallic sulfates are not expected to condense on the fly ash. Once the temperature of the flue gas drops below its dew point, sulfate ions can form, and some of these ions then will form a metallic sulfate. However, this reaction occurs principally in the cold liquid contained in the bubblers, since the temperature of the free stack gas is above the dew point.

The foregoing classification scheme correlates well with other studies of the relationship between trace element enrichment and particle size in fly ash.⁽¹⁹⁾ It was reported that As, Cd, Cr, Ni, Pb, Sb, Se, and Zn show a clear inverse relationship between concentration and particle size. Except for Cr and Ni (in the intermediate group), these

elements are in Class II. No trend with size or poorly defined trends have been reported for Al, Ca, Co, Cu, Fe, K, Mg, Mn, Si, Ti, and V. Of these elements, Cu is in Class II and V is in the intermediate group, but the other nine are in Class I.

A volatilization-condensation or adsorption mechanism also has been proposed to account for the particulate enrichment behavior.⁽¹⁹⁾ Those elements which accumulate on the smaller fly ash particles are assumed to be volatile at the temperature of combustion (about 1800 K); as the flue gas cools, the volatiles condense or adsorb on the fly ash. Since condensation and adsorption are surface phenomena and the smaller particles have a larger surface area per unit mass than do the larger particles, the concentration of condensed elements should be inversely proportional to particle size. Those elements that are not volatile in the combustion zone form the fly ash particles upon which the volatiles condense. The elements that are enriched on the smaller particles usually have boiling points comparable to or less than the 1800 K temperature of the combustion zone.⁽¹⁹⁾

Measurements made on individual fly ash particles using an argon ion etching technique and X-ray spectrometric analysis indicated that several of the elements which show preferential concentration in the finer particles also demonstrate higher concentrations at the particle surface than in the bulk of the particles.

From the observed enrichment-volatilization patterns of the two groups of elements, from volatility data, and from the evidence supporting surface condensation of elements, the following particulate enrichment mechanism is proposed⁽⁴⁴⁾: (1) At maximum furnace temperatures the moderately volatile Class I elements remain condensed as solids or melts and the more highly volatile Class II elements become partially or totally vaporized. (2) As the hot, flowing combustion gases and suspended ash particles are cooled in the boiler, Class II elements adsorb and condense evenly on surfaces of particles consisting mostly of Group I

elements. Because the finer ash particles have a higher surface area per unit mass than coarser particles, they will contain relatively higher concentrations of Group II elements. Many Group II elements are completely condensed, but the most volatile ones (for example, Hg and Se) do not condense completely and pass through the particulate control devices partially in the vapor state. (3) Increasing concentrations of Group II elements in samples collected successively downstream in and near the particulate control devices are a result of the particle-size-dependent collection efficiencies of these devices in which larger particles are more efficiently captured than smaller particles. Thus, the finer particles penetrating the control devices contain higher concentrations of Group II elements than the coarser, collected particles.

9.1 ELEMENT PARTITIONING

The partitioning of the trace elements within the boiler is illustrated in Figures 9-1 through 9-4. Three successive runs were made for each test and the data points plotted on these figures are the arithmetic mean of the element concentrations of the three runs. The individual data for Test 166 are listed on Tables 6-4 through 6-6 and for Test 169 on Tables 7-4 through 7-6.

For Test 169 at Location 31 samples were taken of the furnace bottom ash, the dust collector ash and of the flue gas before and after the collector. For Test 166 at Location 35 the dust collector was built into the backpass of the boiler and it was possible to collect samples only of the combined furnace bottom ash and collector ash and of the flue gas downstream of the collector.

The moderately volatile Class I elements did tend to concentrate in the furnace bottom ash, as proposed in the opening discussion of this section. The concentration of the elements in the bottom ash increased by a factor of from two to six over the concentration in the coal for two-thirds of the elements plotted in Figures 9-1 and 9-2.

Test 166, Location 35

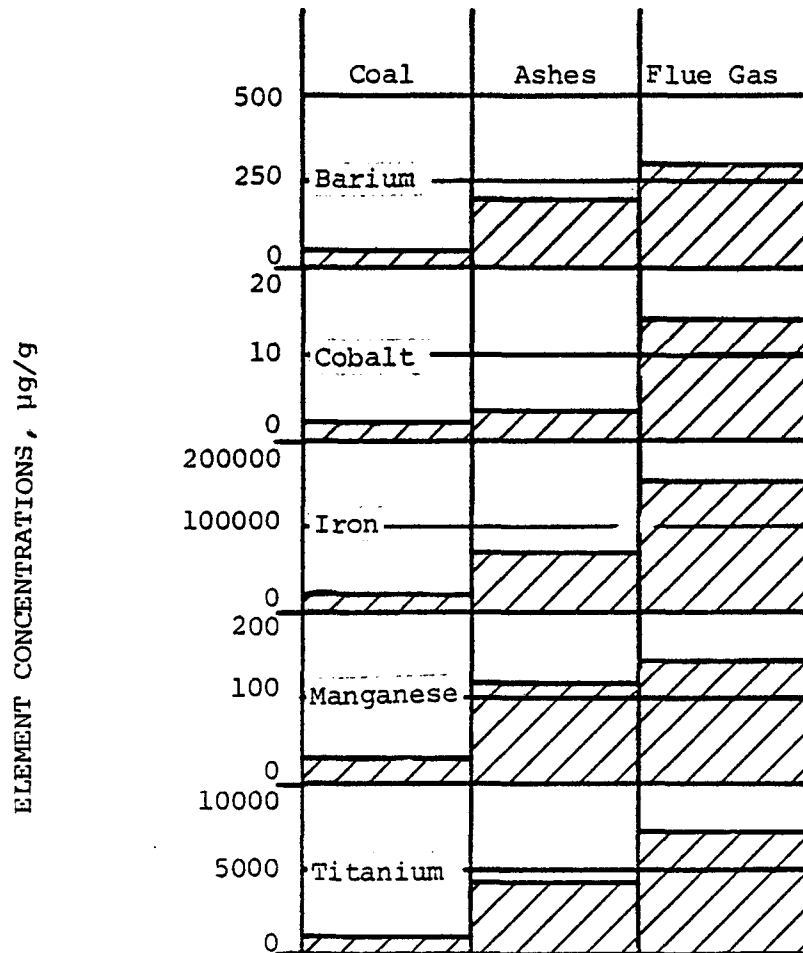


Figure 9-1. Partitioning of moderately volatile elements.

6001-48

Test 169, Location 31

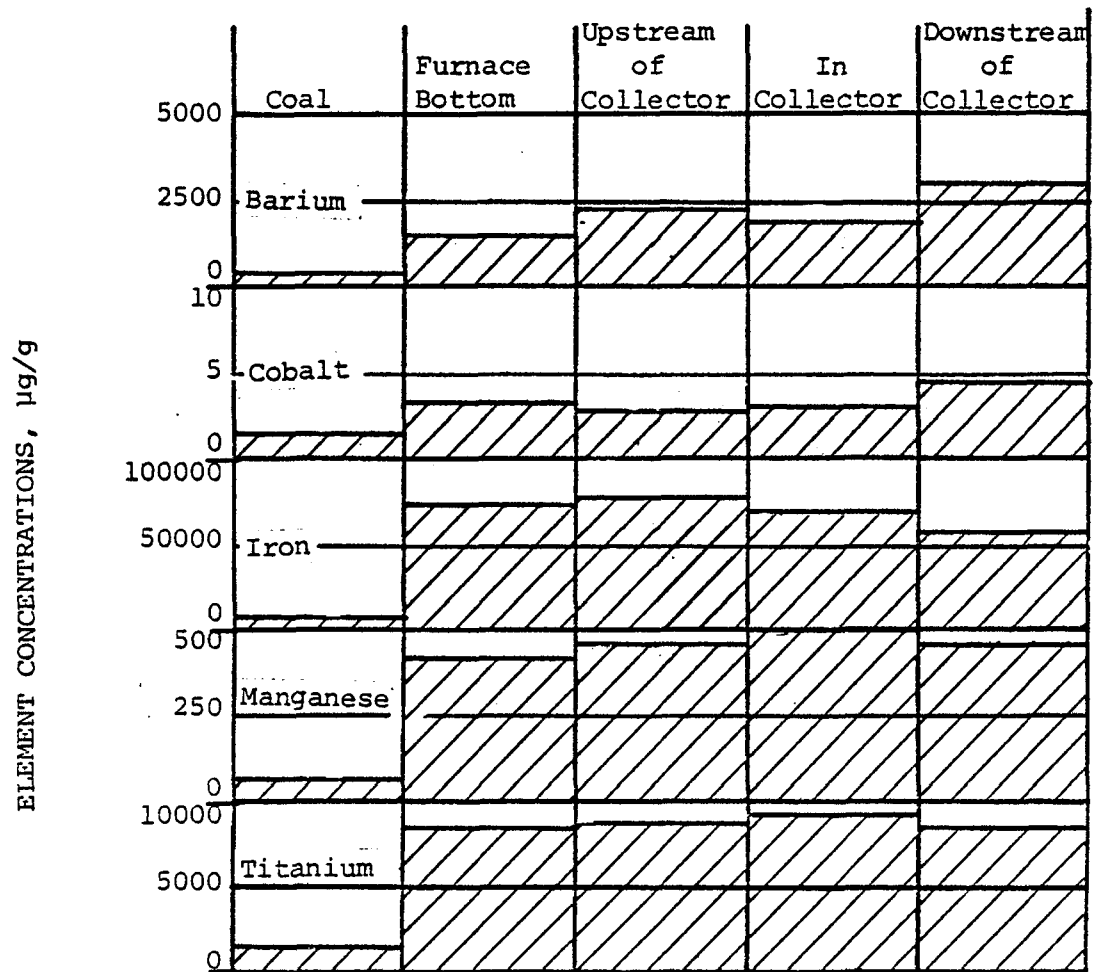


Figure 9-2. Partitioning of moderately volatile elements.

6001-48

Test 166, Location 35

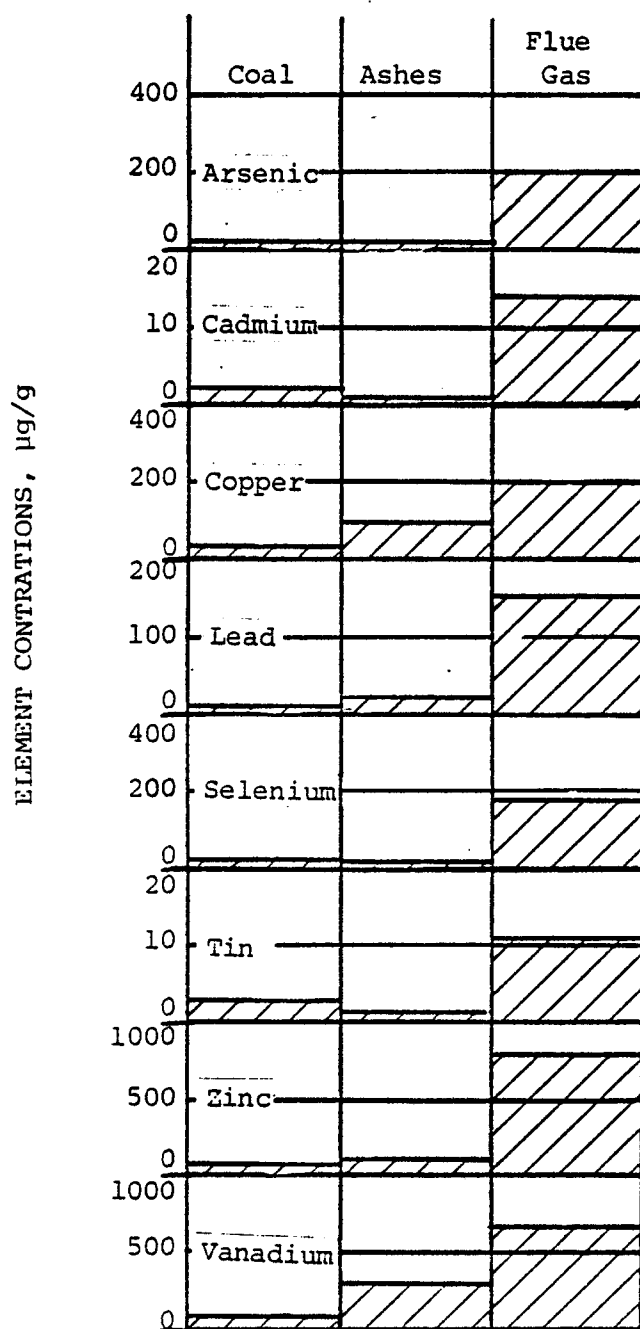


Figure 9-3. Partitioning of highly volatile elements.

6001-48

Test 169, Location 31

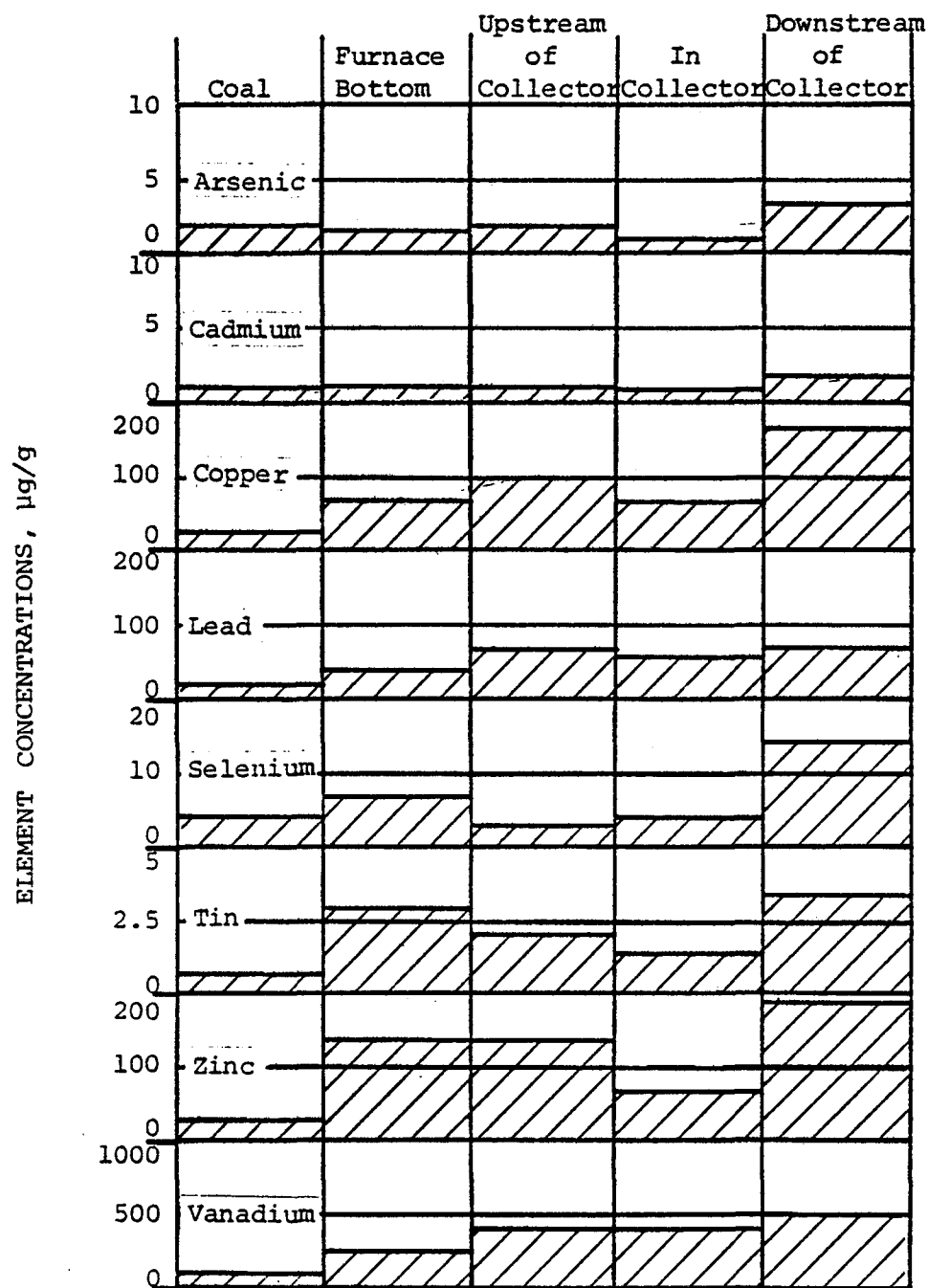


Figure 9-4. Partitioning of highly volatile elements.

6001-48

The concentrations of the various moderately-volatile elements in the flue gas upstream of the collector and downstream of the collector (Figure 9-2) were about the same, as theory predicts. There was no tendency to concentrate in the dust collector, again in conformance with partitioning theory.

The highly-volatile Class II elements generally did not tend to concentrate in the combined bottom and collector ashes of Test 166 shown in Figure 9-3, as would be expected. However, five of the seven Class II elements, copper, lead, selenium, tin, zinc, did concentrate in the bottom ash during Test 169, as indicated in Figure 9-4.

Partitioning theory predicts that the concentration of the light elements in the inlet fly ash upstream of the collector would be greater than in the slag and bottom ash. Figure 9-3 shows that this concentration did occur for four out of the eight elements, arsenic, copper, lead and vanadium. The concentrations of selenium, and tin actually decreased, and the concentrations of cadmium and zinc were unchanged.

In all instances, except the lead concentration of Test 169, the volatile elements concentrated strongly in the fly ash downstream of the collector outlet. Thus, the Class II elements did volatilize upon combustion and did concentrate preferentially on the outlet fly ash, as previously proposed. (12)

Of the Class III elements that were sought, i.e., mercury and chlorine, only mercury could be analyzed. There was insufficient particulate collected to analyze accurately for chlorine. The mercury exhibited two differing behaviors: (1) during Test 166 it increased in concentration downstream of the collector from a level of less than 0.3 $\mu\text{g/g}$ in the coal to a mean of 1.2 $\mu\text{g/g}$ in the flue gas particulate and (2) during Test 169 the concentration was relatively constant at 0.4 $\mu\text{g/g}$ at all locations within the boiler. This difference in the concentrations of mercury is deemed to have been due to the flue

gas temperature. For Test 169 the flue gas temperature was 440 K, while for Test 166 it was only 375 K and more mercury was condensed out and adsorbed onto the particulates.

Vanadium had not been assigned a class because it exhibited a behavior intermediate between Classes I and II. Its behavior is shown on Figures 9-3 and 9-4, and its behavior, indeed, is intermediate between the highly-volatile and the moderately-volatile elements.

9.2 PARTICULATE SIZE

The particulate sizing portion of the field test included thirty runs on ten different boilers. Half of these runs were part of the trace species measurement task and half were part of the combustion modification tests. The results of the combustion modification tests are not discussed here, however References 7 and 8 contain information on the combustion modification tests.

A low speed flow type of cascade impactor that is described in Subsection 3.5 was used to measure particulate aerodynamic diameters. A cyclone was added upstream of the first stage of the impactor when coal was the test fuel. The aerodynamic diameter, D_{50} , cited here is the diameter of a spherical particle of unit density that is collected with 50% efficiency by the impactor stage. In order to forestall particulate rebound and reentrainment, the flue gas flow speed through the impactor was reduced to about two-thirds nominal, and this reduced flow increased the aerodynamic diameters of the stages. The points plotted on the graphs in this section are the aerodynamic diameter cut points of the stages that actually existed during the test.

When analyzing the impactor data it was assumed that all of the mass caught upon an impactation stage consisted of material having aerodynamic diameters equal to or greater than the D_{50} for that stage, and less than the D_{50} for the next higher stage. For the first stage, or the precutter cyclone when one was employed, it was

assumed that all of the captured particulate had aerodynamic diameters greater than, or equal to the D_{50} for the stage or cyclone, but less than an arbitrarily large diameter of 50 μm for oil fuel and 100 μm for coal fuel.

The proportion of particulates in three size categories for the trace tests with oil and coal fuels are listed in Table 9-1. The size category of five-tenths of a micrometer or less was selected because particles that are less than 0.5 μm in size tend to be inhaled and then exhaled, rather than deposited in the alveoli. They do not build up readily in the airways and possibly are not a serious health hazard.

Particulates between 0.5 μm and 50 μm in diameter are inhaled and either filtered out in the airways, deposited in the alveoli or exhaled in various amounts. In this size range particles 3 μm or less are potentially the most hazardous because they tend to penetrate deeply into the respiratory tract. ⁽⁴⁵⁾

The size range of 0.4 to 0.7 μm is of interest because particulates of this size reduce visibility due to Mie scattering of the sunlight by the particulates. This scattering is responsible for a hazy atmosphere.

The combustion of oil fuel produced a larger proportion of particulates having an aerodynamic diameter less than 3 μm than did coal fuel. Thus, more of the particulate emissions from oil is inhaled and exhaled (24%), retained in the respiratory passages (67%), and involved in reduced visibility (7%) than of the emissions from coal.

The chain grate type of coal burner of Test 166 at Location 35 produced more fine particulate (about 36%), than did the pulverizer of Test 169 at Location 31 (about 24%). That the greater proportion of fine particulate was from the chain grate, rather than the pulverizer, was unexpected. The difference in particulate size between the chain grate and pulverizer is not explained easily by the difference in the

TABLE 9-1. PARTICULATE SIZE

OIL FUEL								
Test			Burner or Oil Type	Proportion of Total Weight of Catch				Test Conditions
				Particles Inhaled Then Exhaled <0.5 μm %	Particles In The "Fine" Particulate Size Range <3 μm %	Particles Reducing Visibility by Mie Scattering 0.4-0.7 μm %	Soot Included	
No.	Location	Load GJ/hr (10 ³ lb/hr)						
121-9	29	76 (72)	No. 6	10	68	8	Yes	Baseline
121-10		76 (72)	No. 6	15	70	19	Yes	Baseline
121-11		76 (72)	No. 6	3	30	2	Yes	Baseline
171-6A	20	53 (50)	No. 6	40	73	2	Yes	Baseline
171-6B		53 (50)	No. 6	37	67	2	Yes	Baseline
171-8		54 (64)	No. 6	35	65	2	Yes	Baseline

COAL FUEL								
No.	Location	Load GJ/hr (10 ³ lb/hr)	Burner or Oil Type	Particles Inhaled Then Exhaled <0.5 μm %	Particles In The "Fine" Particulate Size Range <3 μm %	Particles Reducing Visibility by Mie Scattering 0.4-0.7 μm %	Soot Included	Test Conditions
166-5	35	111 (105)	ChGrt	46	65	13	Yes	Baseline, Down- stream of Dust Collector
166-6		111 (105)		25	33	3	Yes	
168-7		116 (110)		6	30	2	Yes	
166-9		106 (100)		5	22	2	Yes	
166-10		116 (110)		5	25	4	Yes	
169-1	31	148 (140)	Pulv.	3	30	1	Yes	Baseline, Up- stream of Dust Collector
169-2		148 (140)		1	30	<1	Yes	Baseline, Down- stream of Dust Collector
169-3		148 (140)		1	11	3	Yes	Baseline, Up- stream of Dust Collector
169-4		148 (140)		1	31	2	Yes	Baseline, Down- stream of Dust Collector
169-6		148 (140)		<1	17	<1	Yes	Baseline, Down- stream of Dust Collector

size of the coal fired, since the larger size crushed coal that was fired on the chain grate would be expected to yield the larger particulate, contrary to observation.

At a diameter of 10 μm and less the order was reversed. The pulverizer produced a greater amount of particulate having a diameter less than 10 μm , 50%, than did the chain grate, 35%. These data are similar to other reported data where 30% of the particulate from a pulverizer was under 10 μm while only 10% from a spreader stoker was under 10 μm in diameter.⁽¹⁰⁾ With pulverized coal, there was a greater proportion of particulate below the 10 μm size cut as compared with the crushed coal.

There was little difference in the proximate analyses of the two coals burned at Location 31, Test 169 and Location 35, Test 166. The averages of the three proximate analyses of the coals was as follows:

Location No. Test No.	Coal		Bottom Ash	
	35 166	31 169	35 166	31 169
Inerts, %	13	11	49	95
Volatile Matter, %	38	39	4	5
Fixed Carbon, %	44	44	45	<1
Heat of Combustion, J/g	26,835	25,576	--	--

However, the proximate analyses of the two ashes were far different. The inerts content of the bottom ash from Test 169 was much higher than that from Test 166, while the carbon content was practically zero. The pulverizer burner completely burned out the carbon, leaving both a bottom ash and fly ash that was almost entirely uncombustible mineral. The chain grate of Test 166 suffered from undersized fans and blocked gas passageways which contributed to the 45% carbon carryover. The pulverizer ash remained or agglomerated into larger size particulates than did the ash from the chain grate.

The smallest proportion of fine particulate was 8% from a spreader stoker tested as part of the combustion modification task. There was no ash analysis nor was the soot blown during this test,

so there can be no direct comparison, as in Tests 166 and 169 above. It was not surprising, however, that a spreader stoker that burned crushed coal partly in suspension, as did the pulverizer, and partly on a grate, as did the chain grate, would produce relatively few fine particulates and many large particulates.

The five individual runs on chain grate-fired coal of Test 166, Runs 5 through 10, are depicted on Figure 9-5. All of the measurements were made downstream of the dust collector, since the dust collector was built into the back-pass of the boiler and the flue gas up stream of the collector was not accessible.

With the exception of Run No. 5 the fine particulate proportion ranged only from 25% to 33%. At 0.5 μ m diameter there was moderate scatter of the data. The relatively large proportion of the mass on the first three stages in Run No. 6 may be due to particulate rebound and reentrainment. The data are typical of a situation where some of the larger particles that belonged on the second through the fourth stages had rebounded and ended up on the filter stage at the outlet end of the impactor. Run No. 5 appears to be a complete anomaly.

The data from Test No. 169, Location 31 are entered on Figure 9-6. The triangles with the base down and connected by the solid curve are data points taken upstream of the cyclone dust collector. The inverted triangles and dashed curves are data taken downstream of the dust collector. The striking feature compared to Figure 9-5 is the much smaller proportion of fine particulate.

On the average, for the five runs, the proportion of fine particulate downstream of the dust collector was larger than the proportion upstream, 26% and 21% respectively. The difference was caused, possibly, by the dust collector's removing more of the larger particulate than the smaller. The amount of particulates from pulverized coal that was 0.5 μ m diam. or smaller was much less across the board than the amount from the chain grate and from oil fuel. The entire particulate size spectrum definitely was weighted toward the larger particulate sizes.

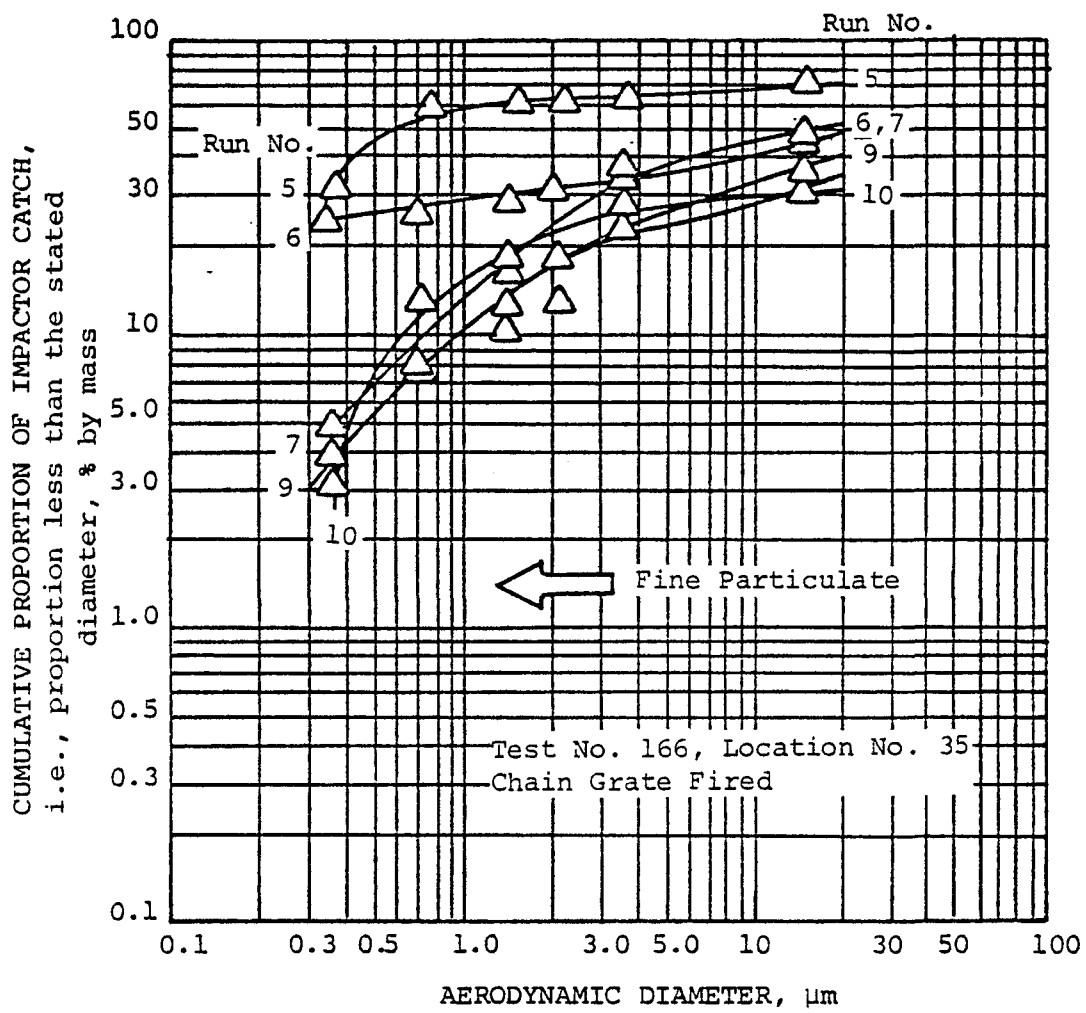


Figure 9-5. Particulate size distribution, coal fuel and chain grate burner.

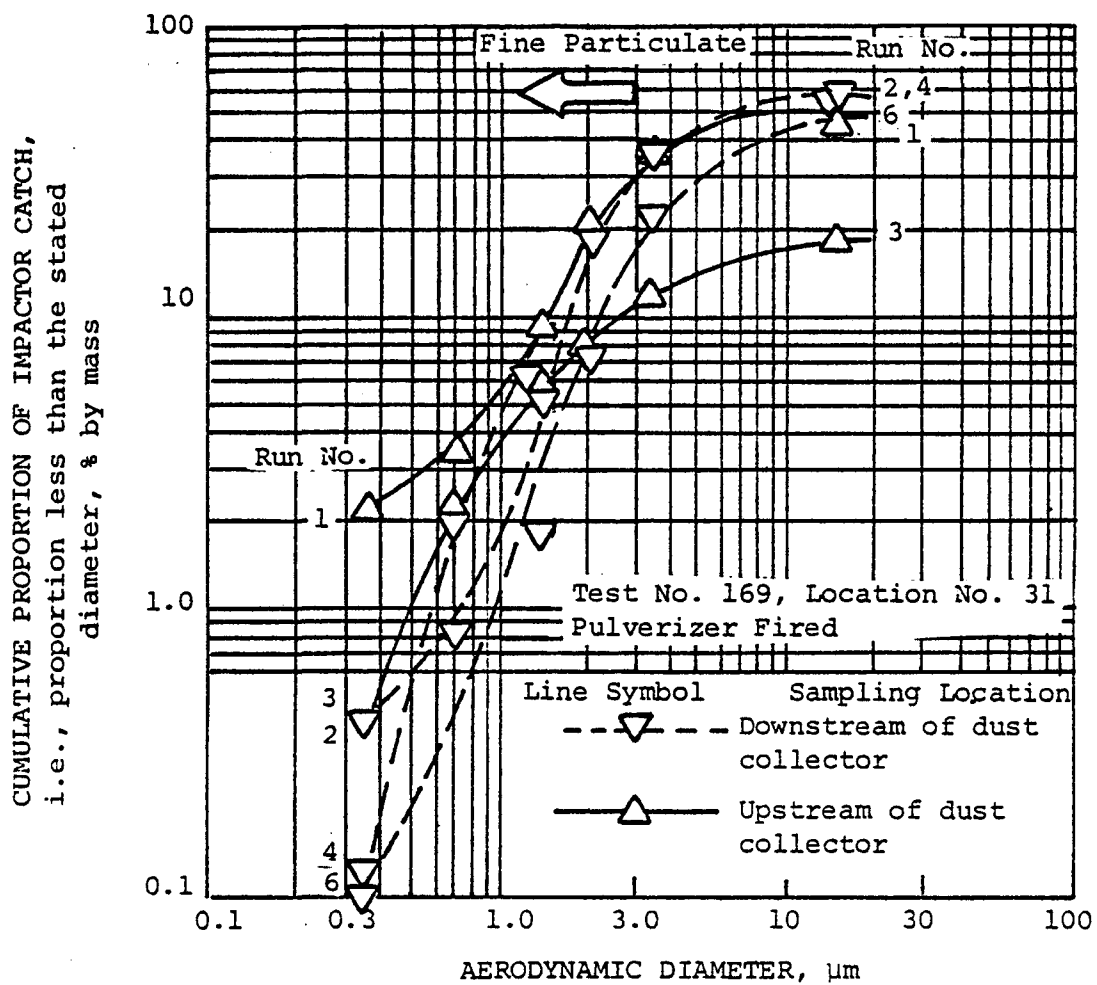


Figure 9-6. Particulate size distribution, pulverized coal fuel.

As with Test No. 166, there were two types of distribution: one convex with a rapid increase in the cumulative proportion up to about 2 μm , and the other s-shaped. The distribution type was not unique to the sample collection site, upstream or downstream; both locations had both types of distribution.

The findings of the size measurements for Tests 121 and 170 with No. 6 oil fuel are plotted on Figures 9-7 and 9-8. It is assumed arbitrarily that 100% of the impactor catch was 50 μm or smaller in diameter; although the largest cut point of the impactor was about 4 μm . The significant difference between these oil data and the coal data shown in the two preceding figures was that the proportion of submicron and fine particulate from oil burning was greater than that from coal by a factor of about 10.

Test 121, Runs 9 through 11, in Figure 9-7 illustrates the size effect of soot blowing during a test. For test runs 121-9 and 121-10 the soot blowing was timed so only the soot deposited during the run was caught by the impactor. For run 121-11, an operational problem caused about 18 hours of soot accumulation to be caught, rather than the 4 hour accumulation of runs 121-9 and 121-10, and the total catch shown in Table 9-2 was 18.99 mg. The result was that the submicron particulates constituted only 3% of the total catch, and a great many more large-size particulates were caught. Apparently there was a significant growth in the size of soot particles by agglomeration over a period of time.

The proportion of the submicron size particulate 0.5 μm or less in diameter and of the fine particulate 3.0 μm or less were about the same from the two runs with light soot. At a diameter of 1.0 μm there was considerable difference in the proportion, but this difference did not persist beyond 2.0 μm .

The amount of fine particulate from the oil-fueled boiler at Location 20, Test 170 was about the same as that shown in Figure 9-7 for Test 121. The individual data points for four of the runs of Test 170 are plotted in Figure 9-8. There was very little scatter in these data, except for Run 5A. The filter stage of Run 5A was damaged during the run and the data were not included in Figure 9-8.

CUMULATIVE PROPORTION OF IMPACTOR CATCH,
i.e., proportion less than the stated
diameter, % by mass

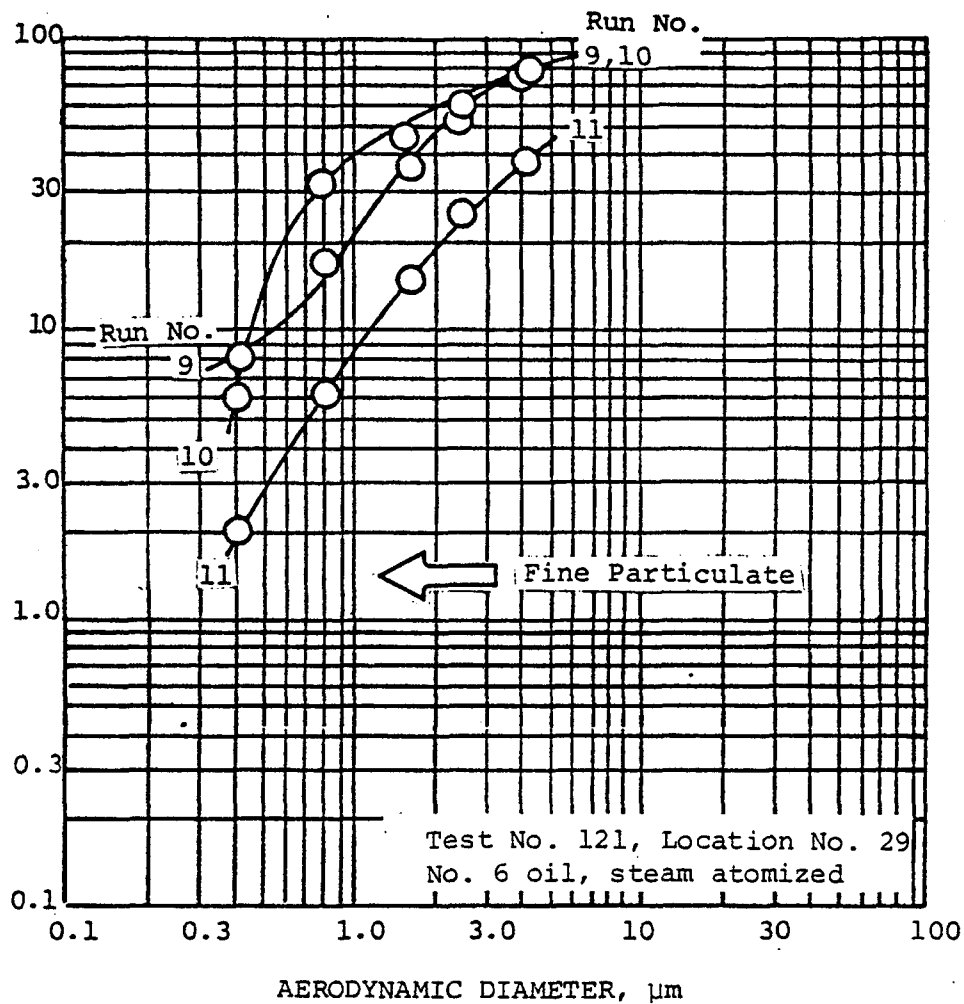


Figure 9-7. Baseline particulate size distribution, No. 6 oil fuel.

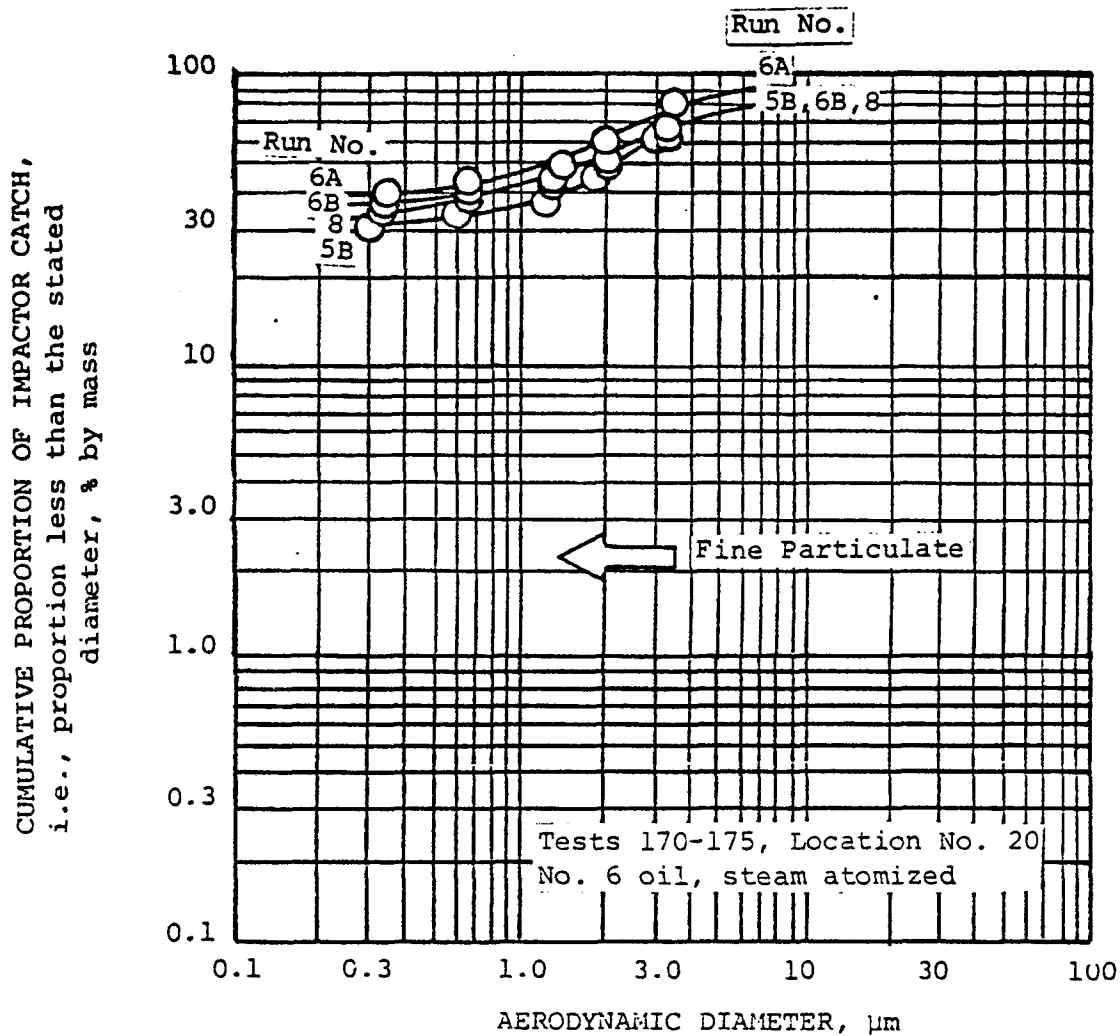


Figure 9-8. Baseline particulate size distribution, No. 6 oil.

Table 9-2. CASCADE IMPACTOR DATA SUMMARY

Test No.	Loc. No.	Fuel Type	Burner Type	Test Load GJ·hr ⁻¹	Impact. Flow cm ³ ·s ⁻¹	Actual D ₅₀ of Stage No.					D ₅₀ Cycl. µm	Cyclone, Stage and Filter Catch					Filter mg	Total Catch mg	Comments	
						Stage No.						Cyclone mg	Stage No.							
						1 µm	2 µm	3 µm	4 µm	5 µm			1 mg	2 mg	3 mg	4 mg				5 mg
111	27	PS300	Steam	90	35.4	2.9	1.7	1.2	0.58	0.29	--	None	0.368	0.148	0.240	0.272	0.216	0.864	2.11	Baseline
112	27	PS300	Steam	90	37.7	2.8	1.7	1.1	0.56	0.28	--	None	0.038	0.246	0.444	0.296	0.304	M	1.33	Filter destroyed
130	28	No. 6	Steam	31	11.8	5.0	3.0	2.0	1.0	0.4	--	None	2.064	1.152	0.896	0.880	0.784	0.328	6.10	Baseline
121-9	29	No. 6	Steam	76	17.8	4.1	2.4	1.6	0.81	0.41	--	None	1.00	1.08	1.21	0.992	0.488	0.400	5.17	Light soot
121-10	29	No. 6	Steam	74	20.0	3.85	2.31	1.54	0.77	0.38	--	None	1.82	2.20	0.616	1.06	2.17	0.560	8.62	Light soot
121-11	29	No. 6	Steam	126	17.9	4.1	2.4	1.6	0.81	0.41	--	None	11.7	2.62	1.84	1.64	0.848	0.348	18.99	Heavy soot
139-5	30	Coal	Spread	53	46.5	2.5	1.5	1.0	0.5	0.25	10.9	75.1	8.33	5.49	0.488	0.396	0.528	0.120	90.5	Baseline
156-2	13	Coal	Pulv.	420	51.5	2.5	1.4	0.96	0.48	0.24	10.4	52.6	57.7	34.2	8.82	6.69	3.04	0.236	163	Baseline
166-3	35	Coal	Grate	116	24.6	3.5	2.1	1.4	0.70	0.35	15.6	10.39	1.056	0.780	0.660	0.340	0.600	0.572	14.60	Baseline no soot
166-5	35	Coal	Grate	111	22.2	3.6	2.2	1.5	0.73	0.36	15.8	32.3	6.54	2.75	1.176	0.714	32.20	33.91	109.8	Toxic with soot
166-6	35	Coal	Grate	111	25.5	3.4	2.0	1.4	0.68	0.34	14.7	30.01	6.18	2.32	1.01	1.33	0.916	13.74	55.51	Toxic with soot
166-7	35	Coal	Grate	115	23.6	3.5	2.1	1.4	0.71	0.35	15.3	13.06	3.22	4.60	1.38	1.21	0.772	1.22	25.46	Toxic with soot
168-8	35	Coal	Grate	103	23.6	3.5	2.1	1.4	0.71	0.35	15.3	10.82	0.200	0.276	0.472	2.10	3.26	1.29	18.42	Low NOx, no soot
168-9	35	Coal	Grate	106	24.1	3.5	2.1	1.4	0.70	0.35	15.2	19.99	3.30	4.01	0.916	0.692	1.304	1.24	31.40	Toxic with soot
168-10	35	Coal	Grate	116	24.1	3.5	2.1	1.4	0.70	0.35	15.2	34.15	0.768	3.42	2.58	1.20	4.88	1.55	48.53	Toxic with soot
160-5	36	No. 2	Steam	58	28.3	3.2	1.9	1.3	0.64	0.32	--	None	96.9	7.55	0.408	0.756	0.008	0.368	105.6	Lower Load
162-11	36	No. 2	Steam	65	28.3	3.2	1.9	1.3	0.64	0.32	--	None	5.60	0.148	0.064	1.032	0.024	0.192	70.6	Low NOx
162-36	36	No. 2	Steam	65	28.3	3.2	1.9	1.3	0.64	0.32	--	None	10.6	3.57	0.788	0.62	0.034	0.20	15.842	Baseline
169-1	31	Coal	Pulv.	148	23.7	3.53	2.12	1.41	0.71	0.35	15.3	289.2	48.02	92.46	55.95	33.24	6.48	11.91	537.27	Toxic, Upstream dust collector
169-2	31	Coal	Pulv.	148	25.7	3.39	2.03	1.36	0.68	0.34	15.4	64.49	32.55	26.90	19.60	4.82	2.15	0.600	151.112	Toxic, Downstream dust collector
169-3	31	Coal	Pulv.	148	25.7	3.39	2.03	1.36	0.68	0.34	14.7	67.83	5.49	2.89	2.05	2.74	1.50	0.336	82.92	Toxic, Upstream dust collector
169-4	31	Coal	Pulv.	148	26.4	3.35	2.01	1.34	0.67	0.34	14.5	72.39	35.20	32.00	19.42	6.73	3.04	0.208	168.99	Toxic, Downstream dust collector
169-6	31	Coal	Pulv.	148	23.7	3.53	2.12	1.41	0.71	0.35	15.3	71.89	40.63	20.96	8.11	1.36	1.02	0.156	144.13	Toxic, Downstream dust collector
171-6A	20	No. 6	Steam	53	26.1	3.36	2.02	1.35	0.67	0.34	--	None	0.588	0.616	0.332	0.172	0.140	1.160	3.008	Baseline, Toxic
171-6B	20	No. 6	Steam	53	27.6	3.27	1.96	1.31	0.66	0.33	--	None	1.052	0.480	0.256	0.172	0.068	1.172	3.200	Baseline, Toxic
171-8	20	No. 6	Steam	54	26.1	3.36	2.02	1.35	0.67	0.34	--	None	1.060	0.501	0.256	0.168	0.108	1.120	3.213	Baseline, Toxic
170-5A	20	No. 6	Steam	68	29.3	3.18	1.91	1.27	0.64	0.32	--	None	1.792	0.852	0.512	0.164	0.256	0.288	3.864	Baseline
175-5B	20	No. 6	Steam	67	34.5	2.93	1.76	1.17	0.59	0.29	--	None	3.824	1.660	0.924	0.372	0.312	3.158	10.250	Registers
176-5	37	No. 6	Steam	34	22.6	3.62	2.17	1.45	0.72	0.36	--	None	2.812	1.616	0.668	0.456	0.312	2.700	8.564	Baseline
179-4	37	No. 6	Steam	34	22.7	3.61	2.17	1.44	0.72	0.36	--	None	3.112	1.372	0.596	0.332	0.196	2.344	7.952	Low NOx

The complete cascade impactor test data for both the trace species tests and the combustion modification tests are tabulated in Table 9-2.

9.3 PARTICULATE ENRICHMENT

There was an inverse relationship between the element concentrations and the particulate sizes for the highly-volatile elements of Class I, as predicted by the enrichment theory discussed in the introduction to this section. The less volatile Class I elements exhibited little or no enrichment, again in accordance with theory.

The results of the particulate enrichment portion of the Tests 166 and 169 are shown in Figures 9-9 through 9-12. The enrichment of the volatile elements, such as antimony, cadmium, chromium, lead, and zinc, was pronounced during Test 169, as indicated in Figure 9-12. During Test 166 the enrichment of cadmium, lead, and zinc was erratic, as shown in Figure 9-11, but the general trend was in accordance with enrichment theory.

Although the less volatile Class I elements did experience some enrichment of the fine particulate, as shown in Figures 9-9 and 9-10, the trend was less pronounced than it was for the more volatile Class II elements.

Figures 9-10 and 9-12 illustrate the effect of a dust collector on particulate enrichment. The effect with both classes of element was to increase the enrichment of the smaller size particulates, except for copper, lead and manganese. Manganese was unaffected by the collector, while the concentrations of copper and lead in the smaller particulates was reduced, rather than increased, by the dust collector.

A phenomena that occurred in the particulate enrichment graphs was the peak in concentration that occurred for certain elements at a diameter of $1.5 \mu\text{m}$. These elements were cadmium, chromium, lead, and zinc. The enrichment of these four elements was somewhat bimodal and reminds one of the well-known bimodal mass-size distribution of urban aerosols.⁽⁴⁶⁾ The two phenomena probably are not related, however, since the urban aerosol mass-size concentration peaks at diameters of 0.5 and $10 \mu\text{m}$, rather than near $15 \mu\text{m}$.

Test 166, Location 35

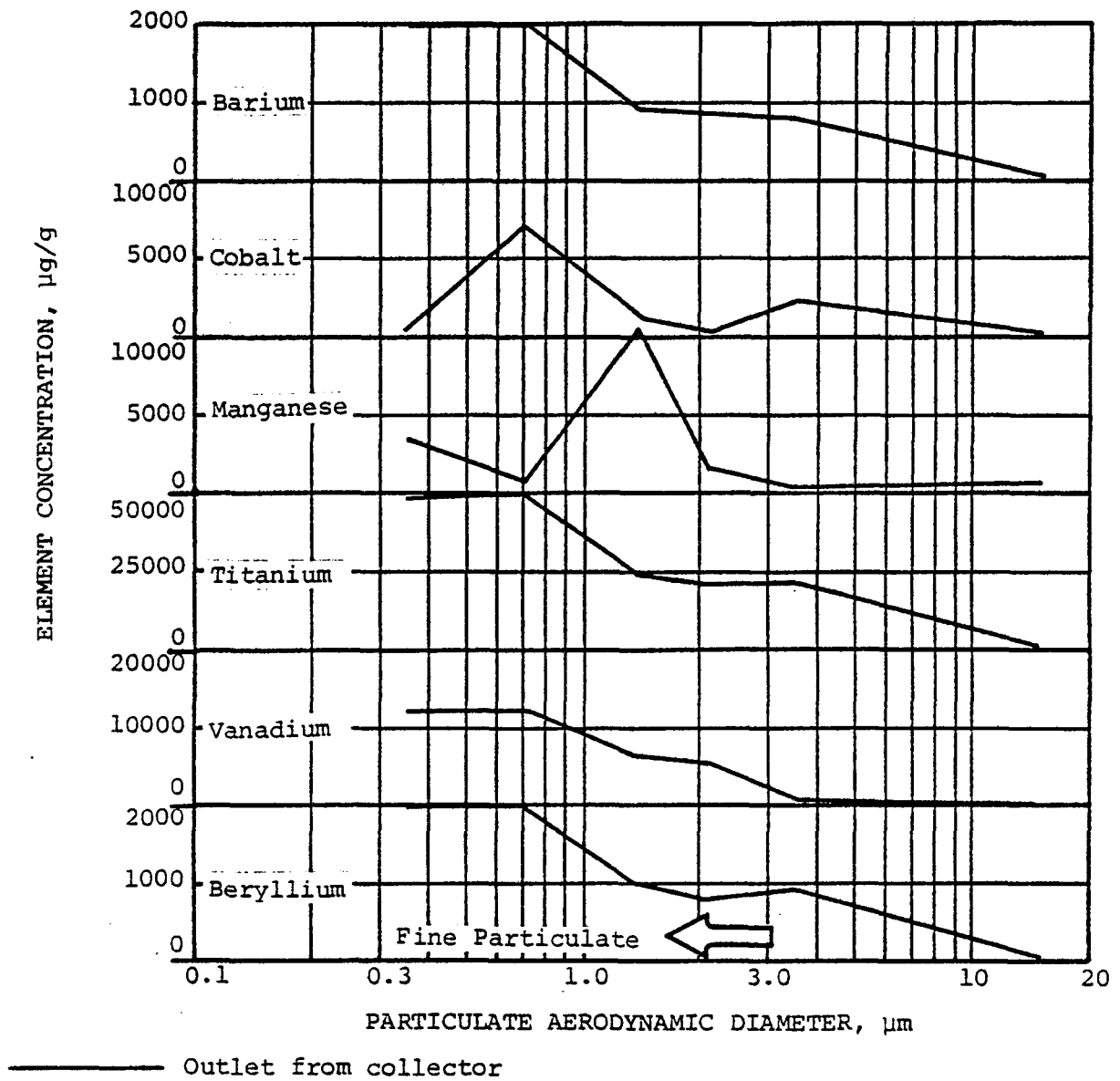


Figure 9-9. Particulate enrichment by moderately volatile elements.

Test 169, Location 31

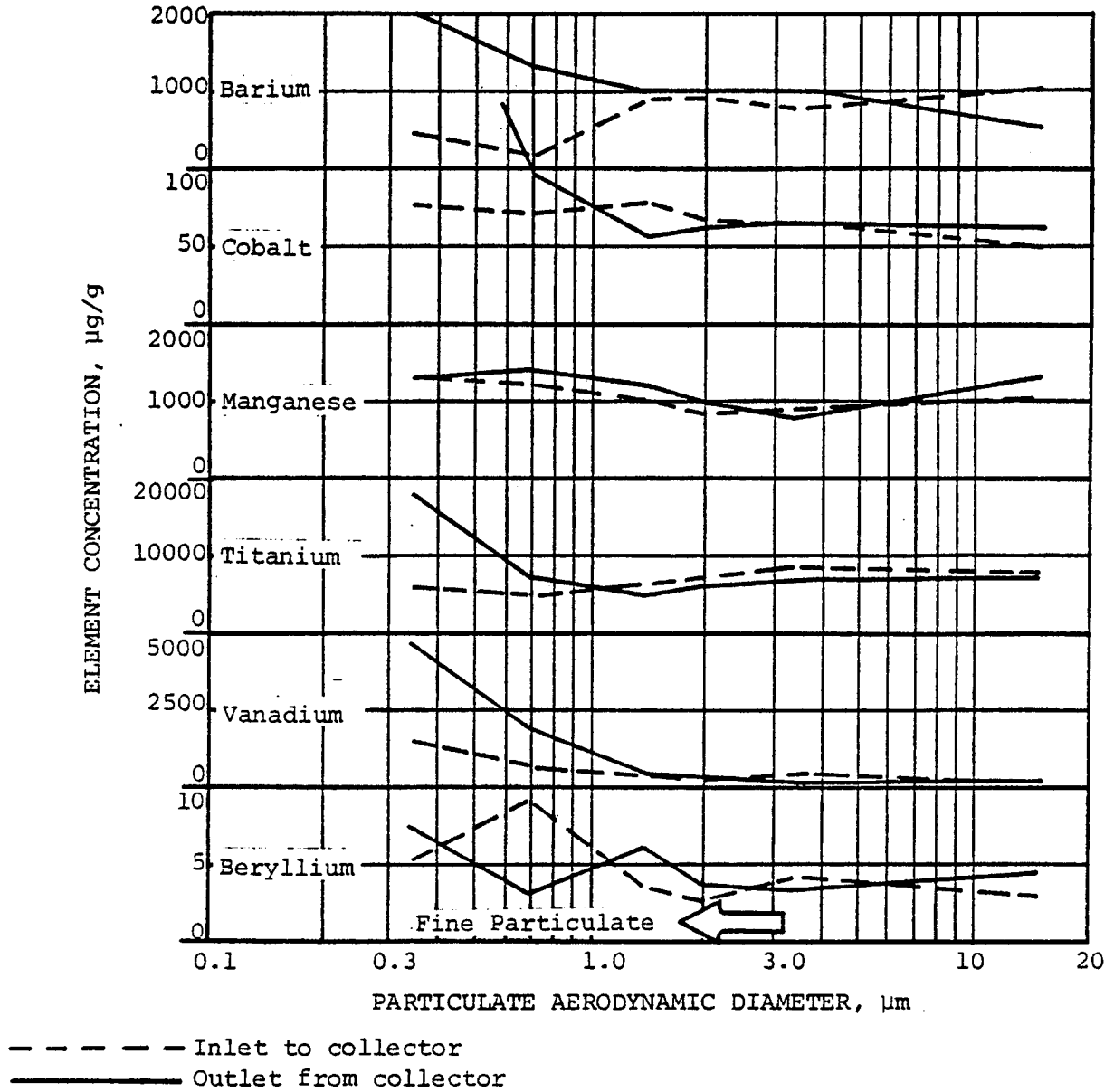


Figure 9-10. Particulate enrichment by moderately volatile elements.

Test 166, Location 35

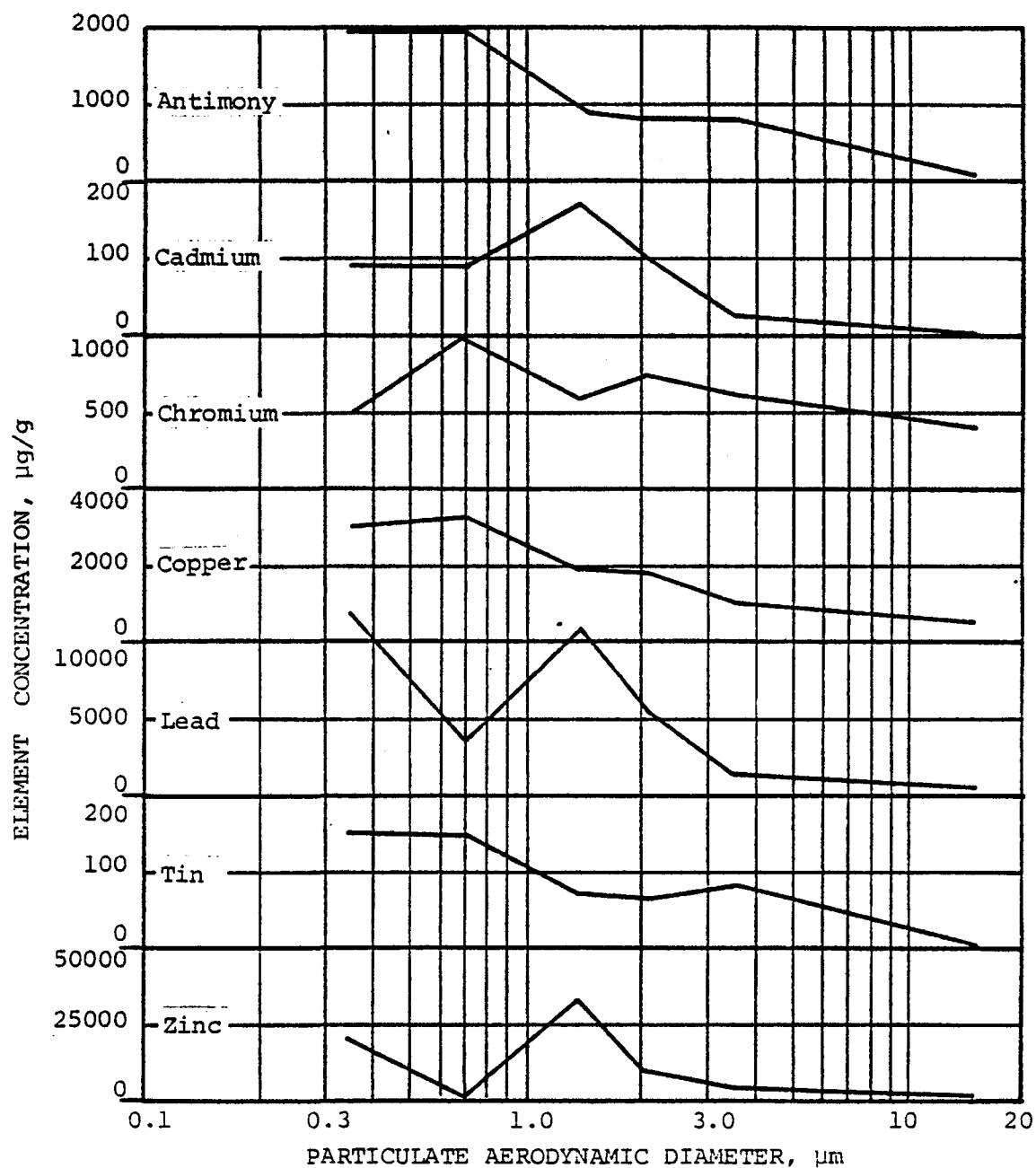


Figure 9-11. Particulate enrichment by highly volatile elements.

Test 169, Location 31

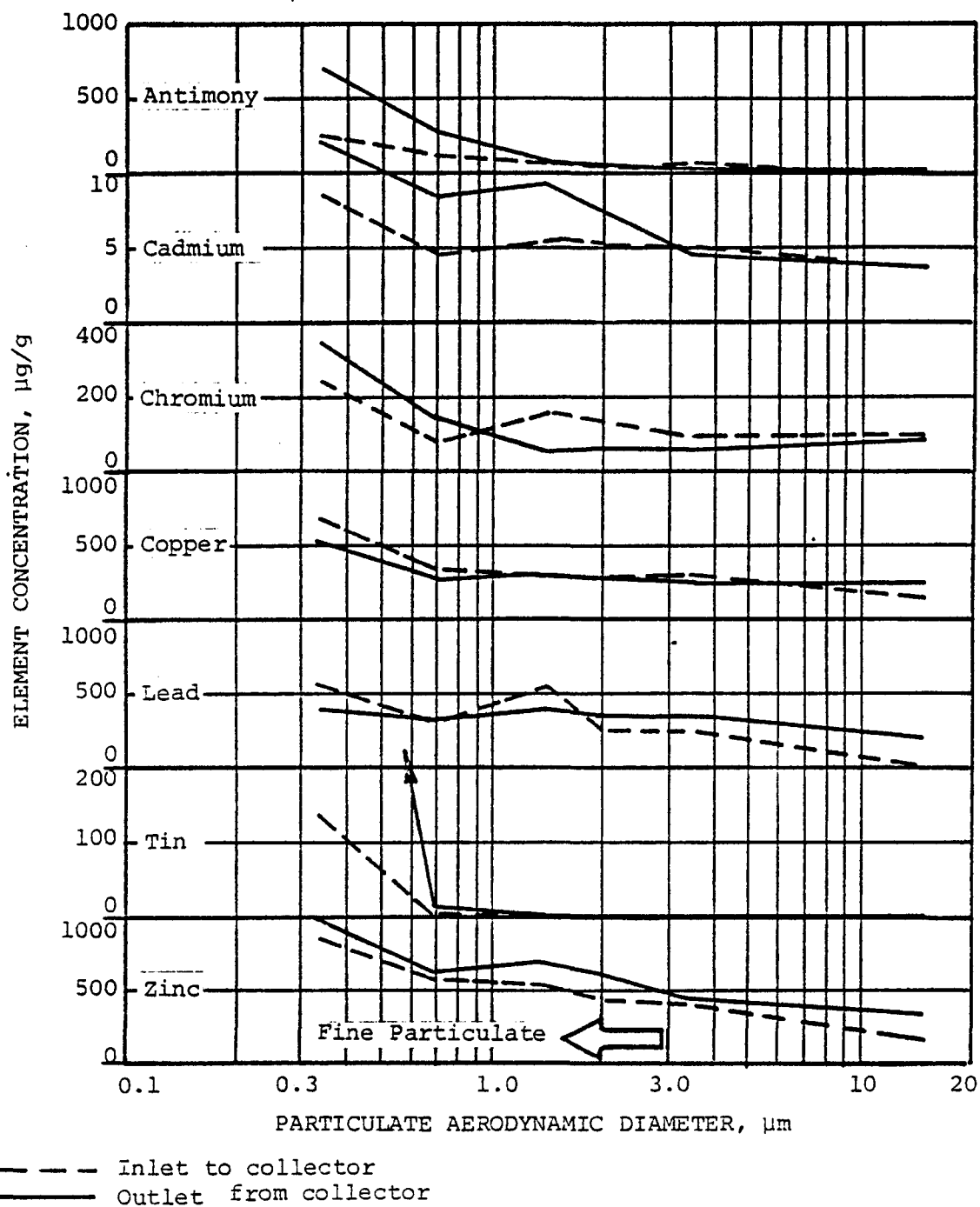


Figure 9-12. Particulate enrichment by highly volatile elements.

6001-48

The particulate size data for the two tests are tabulated in Tables 9-3 and 9-4. Each test consisted of three runs with a cascade impactor that was made up of a cyclone followed by five collection stages, as is described in Section 4. An individual run did not collect enough particulate for an accurate analysis, so the catch of a given stage for all three runs were combined to yield an adequate quantity of sample for analysis. Consequently, the entries in the tables are an average concentration for a set of three successive runs.

No concentrations are reported for the backup filters, because the mass of the particulate catch was so small that the concentration of the trace species collected was indistinguishable from the background of the filter impurities.

TABLE 9-3. PARTICULATE SIZE AND ENRICHMENT

Test No. 169, Location No. 31

Inlet to Dust Collector

Trace Species	Concentration, $\mu\text{g/g}$					
	Aerodynamic Diameter, μm					
	Cyclone 15 μm	Stage 1 3.4 μm	Stage 2 2.1 μm	Stage 3 1.4 μm	Stage 4 0.69 μm	Stage 5 0.34 μm
Antimony*	<35	<130	<66	<120	<210	<430
Barium*	1,100	770	900	880	<230	<450
Beryllium†	2.9	4.2	2.6	3.6	9.1	<10
Cadmium†	3.9	5.0	5.2	5.4	4.5	8.6
Chromium*	110	110	62	170	83	240
Cobalt†	49	65	65	78	69	77
Copper†	170	310	280	300	340	680
Lead†	10	270	260	570	300	560
Manganese†	1,100	900	800	1,000	1,200	1,300
Nickel*	330	47	40	165	62	260
Tin†	1.4	4.0	3.0	3.0	3.3	140
Titanium*	7,700	8,400	7,000	6,100	5,400	<11,000
Vanadium*	150	<850	<430	<760	<1,400	<2,800
Zinc*	180	400	440	540	580	850

Outlet From Dust Collector

Trace Species	Concentration, $\mu\text{g/g}$					
	Aerodynamic Diameter, μm					
	Cyclone 15 μm	Stage 1 3.44 μm	Stage 2 2.06 μm	Stage 3 1.38 μm	Stage 4 0.69 μm	Stage 5 0.34 μm
Antimony*	<61	<59	<83	<150	<560	<1,400
Barium*	570	1,100	1,100	1,000	1,300	2,200
Beryllium*	4.3	3.3	3.5	6.3	<6.3	<15
Cadmium†	3.9	4.6	7.1	9.1	8.3	12
Chromium*	92	58	62	55	<140	<360
Cobalt†	63	66	62	57	97	1,100
Copper†	260	250	280	300	280	520
Lead†	200	360	360	400	320	410
Manganese†	1,300	780	1,000	1,200	1,400	1,300
Nickel*	76	78	71	77	310	<340
Tin†	2.2	3.3	4.4	5.7	10	900
Titanium*	6,900	6,600	5,700	4,800	<14,000	<36,000
Vanadium*	<410	<390	<550	<1,000	<3,700	<9,300
Zinc*	340	450	610	690	620	1,000

* Determined by flame atomic absorption.

† Determined by graphite furnace atomic absorption.

6001-48

TABLE 9-4. PARTICULATE SIZE AND ENRICHMENT
Test No. 166, Location No. 35
Outlet From Dust Collector

Trace Species	Concentration, $\mu\text{g/g}$					
	Aerodynamic Diameter, μm					
	Cyclone 15 μm	Stage 1 3.5 μm	Stage 2 2.1 μm	Stage 3 1.4 μm	Stage 4 0.70 μm	Stage 5 0.35 μm
Antimony*	<140	<1,600	<1,600	<1,800	<3,900	<3,800
Barium*	230	<1,800	<1,700	<1,900	<4,100	<4,000
Beryllium*	12	<18	<18	27	79	51
Cadmium [†]	8.1	23	98	170	95	94
Chromium*	400	610	740	580	1,100	<930
Cobalt [†]	135	2,300	300	1,000	7,100	420
Copper [†]	530	1,100	1,700	1,800	3,300	2,900
Lead [†]	580	1,300	5,300	11,000	3,600	12,000
Manganese [†]	710	400	1,700	11,000	840	3,300
Nickel*	450	490	<390	1,000	1,800	<930
Tin [†]	4.1	84	64	69	150	150
Titanium*	<3,700	<42,000	<41,000	<46,000	<99,000	<96,000
Vanadium*	<430	<1,000	<11,000	<12,000	<26,000	<25,000
Zinc*	1,200	4,000	9,400	34,000	1,200	20,000

* Determined by flame atomic absorption.

[†] Determined by graphite furnace atomic absorption.

SECTION 10.0

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SECTION 11.0

CONVERSION FACTORSSI Units to Metric or English Units

<u>To Obtain</u>	<u>From</u>	<u>Multiply By</u>	<u>To Obtain ppm at 3% O₂ of</u>	<u>Multiply Concentration in ng/J by</u>
g/Mcal	ng/J	0.004186		
10 ⁶ Btu	GJ	0.948	<u>Natural Gas Fuel</u>	
MBH/ft ²	GJ·hr ⁻¹ ·m ⁻²	0.08806	CO	3.23
MBH/ft ³	GJ·hr ⁻¹ ·m ⁻³	0.02684	HC	5.65
Btu	gm cal	3.9685 x 10 ⁻³	NO or NOx	1.96
10 ³ lb/hr* or MBH	GJ/hr	0.948	SO ₂ or SOx	1.41
lb/MBtu	ng/J	0.00233	<u>Oil Fuel</u>	
ft	m	3.281	CO	2.93
in	cm	0.3937	HC	5.13
ft ²	m ²	10.764	NO or NOx	1.78
ft ³	m ³	35.314	SO ₂ or SOx	1.28
lb	Kg	2.205	<u>Coal Fuel</u>	
Fahrenheit	Celsius	$t_F = 9/5(t_C) + 32$	CO	2.69
	Kelvin	$t_F = 1.8K - 460$	HC	4.69
psig	Pa	$P_{psig} = (P_{pa})(1.450 \times 10^{-4}) - 14.7$	NO or NOx	1.64
psia	Pa	$P_{psia} = (P_{pa})(1.450 \times 10^{-4})$	SO ₂ or SOx	1.18
iwg (39.2°F)	Pa	$P_{iwg} = (P_{pa})(4.014 \times 10^{-3})$	<u>Refinery Gas Fuel (Location 33)</u>	
			CO	3.27
			HC	5.71
			NO or NOx	1.99
			SO ₂ or SOx	1.43
			<u>Refinery Gas Fuel (Location 39)</u>	
			CO	3.25
			HC	5.68
			NO or NOx	1.98
			SO ₂ or SOx	1.42

*lb/hr of equivalent saturated steam

English and Metric Units to SI Units

<u>To Obtain</u>	<u>From</u>	<u>Multiply By</u>	<u>To Obtain</u> <u>ng/J of</u>	<u>Multiply Concentration</u> <u>in ppm at 3% O₂ by</u>
ng/J	lb/MBtu	430	<u>Natural Gas Fuel</u>	
ng/J	g/Mcal	239	CO	0.310
GJ·hr ⁻¹ ·m ⁻²	MBH/ft ²	11.356	HC	0.177
GJ·hr ⁻¹ ·m ⁻³	MBH/ft ³	37.257	NO or NOx (as equivalent NO ₂)	0.510
GJ/hr	10 ³ lb/hr [*] or 10 ⁶ Btu/hr	1.055	SO ₂ or SOx	0.709
m	ft	0.3048	<u>Oil Fuel</u>	
cm	in	2.54	CO	0.341
m ²	ft ²	0.0929	HC	0.195
m ³	ft ³	0.02832	NO or NOx (as equivalent NO ₂)	0.561
Kg	lb	0.4536	SO ₂ or SOx	0.780
Celsius	Fahrenheit	$t_c = 5/9 (t_F - 32)$	<u>Coal Fuel</u>	
Kelvin		$t_K = 5/9 (t_F - 32) + 273$	CO	0.372
Pa	psig	$P_{pa} = (P_{psig} + 14.7) (6.895 \times 10^3)$	HC	0.213
Pa	psia	$P_{pa} = (P_{psia}) (6.895 \times 10^3)$	NO or NOx (as equivalent NO ₂)	0.611
Pa	iwg (39.2°F)	$P_{pa} = (P_{iwg}) (249.1)$	SO ₂ or SOx	0.850
<u>*lb/hr of equivalent saturated steam</u>			<u>Refinery Gas Fuel (Location 33)</u>	
			CO	0.306
			HC	0.175
			NO or NOx (as equivalent NO ₂)	0.503
			SO ₂ or SOx	0.700
			<u>Refinery Gas Fuel (Location 39)</u>	
			CO	0.308
			HC	0.176
			NO or NOx (as equivalent NO ₂)	0.506
			SO ₂ or SOx	0.703

TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)			
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16. ABSTRACT The report gives results of the sampling of four coal-fired industrial boilers to determine the emissions of 19 trace and minor elements and polycyclic matter (POM). The trace and minor element emissions were related to total quantities of each element present in the fuel by examining the degree of mass balance and element partitioning based on fuel input and element output in furnace deposits, flyash, and flue gas vapor. The tendency of volatile elements for enrichment of finer particulate was examined by analysis of cascade impactor samples. Measured output of elements classified as high in volatility tended to be less than the fuel input, attributed to possible low collection efficiency of vapor-phase element sampling equipment. These same elements were found to be more highly concentrated in the flyash as opposed to furnace deposits and to have higher concentrations in the smaller particle sizes. Elements classed as medium or low in volatility tended to be more uniformly distributed with respect to both partitioning in the boilers and particle size. Mass output results for these elements frequently exceeded coal input, indicating possible sample contamination by boiler or sampling system construction materials. The presence of four specific POM compounds was indicated in the coal, ashes, and stack gases, but results were highly variable.			
17. KEY WORDS AND DOCUMENT ANALYSIS			
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Tests		Air Pollution Control	13B 14B
Boilers Combustion		Stationary Sources	13A 21B
Coal		Trace Elements	21D
Chemical Analysis		Polycyclic Organic	07D
Organic Compounds		Matter	07C
Polycyclic Compounds			
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