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MEASUREMENT OF CHEMICAL EMISSIONS UNDER THE INFLUENCE OF LOW-NO$_x$ COMBUSTION MODIFICATIONS

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Submitted to
Southern Company Services, Inc.

~~Final Report~~

Contract C-91-000017
SRI Project 7436

SRI-ENV-92-796-7436
October 8, 1993

Southern Research Institute

MEASUREMENT OF CHEMICAL EMISSIONS UNDER THE INFLUENCE OF LOW-NO_x COMBUSTION MODIFICATIONS

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Prepared by

Edward B. Dismukes
Southern Research Institute
P. O. Box 55305
Birmingham, Alabama 35255

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SUMMARY

This report describes an investigation of the emission of hazardous air pollutants at a coal-burning electric power plant identified (for reasons given below) as EPRI PISCES Site 110. The sampling of air toxics was performed at the power plant during September 1991 and January 1992; the analytical work was in progress from September 1991 until September 1992. Southern Company Services, Inc., was the immediate sponsor of the this work. Financial support, however, came from the Electric Power Research Institute (EPRI) and the U.S. Department of Energy (DOE). This research was related to EPRI's measurement program on hazardous air pollutants from electric power stations, known as PISCES (Power Plant Integrated Systems: Chemical Emission Studies). The test site was designated as Site 110 by EPRI; the sampling and analytical strategies were consistent with protocols developed for use in the PISCES program. This research was also related to the DOE's role in the response to the Congressional mandate for the control of hazardous air pollutants under Title III of the Clean Air Act Amendments of 1990.

Two features of the plant that were of particular interest in this investigation of hazardous air pollutants (also known as "air toxics") are 1) the modification of the combustion process to reduce the emission of nitrogen oxides and 2) the use of two electrostatic precipitators (ESPs) in a tandem arrangement, on the hot side and the cold side of the air heater, for the control of particulate emissions. The specific questions to be addressed by this research project were as follows:

1) How does the change to low-NO_x firing alter the emission of hazardous air pollutants?

2) What degree of control over the emission of air toxics is exercised by the hot-side ESP?

3) What added benefit toward the control of emissions does the cold-side ESP provide?

The principal types of substances treated as air toxics in this project were the following:

Trace elements, mainly metals. Most of the metals were from the list in the Clean Air Act Amendments; they consisted of antimony, arsenic, beryllium, cadmium,

cobalt, chromium, lead, manganese, mercury, nickel, and selenium. Four other metals — barium, copper, molybdenum, and vanadium — were added to that list. Collectively, these elements were of interest insofar as their total concentrations in various streams were concerned and also insofar as their concentrations in gas streams were divided between the particulate and gas phases. Individually, arsenic, chromium, and mercury were to be determined as different species — arsenic in the trivalent and pentavalent states, As(III) and As(V), having somewhat uncertain relative toxicities; chromium in hexavalent form, Cr(VI), which is acutely carcinogenic; and mercury in an oxidized state or the elemental state, which determine whether the effects of mercury emission are likely to occur locally or only at a remote location.

Inorganic gases consisting of SO_x, HF, HCl, HCN, and ammonia (NH_3). The first three of these gases are the common forms in which sulfur, fluorine, and chlorine are emitted from a coal combustor. The latter two gases contain nitrogen in reduced states in distinction to the oxidized states found in NO_x, the predominant form of emission of nitrogen other than N_2. The emission of the latter two gases was presumed to be the possible result of staged combustion to reduce NO_x emissions.

Aldehydes (notably formaldehyde) and ketones, which are partially oxygenated hydrocarbons. These compounds are possible emissions resulting from the partial oxidation of more complex structures.

Volatile organic compounds, which are generally organic compounds with boiling points below 100 °C. Formally speaking, volatile organics would include formaldehyde and some of the other aldehydes and ketones. Practically speaking, however, these compounds exclude formaldehyde and may be defined as those compounds that can be collected under the specific sampling conditions employed in EPA's Volatile Organics Sampling Train (VOST). The two specific volatiles of primary interest were the two simple aromatic hydrocarbons — benzene and toluene.

Semi-volatile organic compounds, which generally have boiling points above 100 °C. The compounds of paramount interest in this group are known as polynuclear aromatic hydrocarbons (PAHs); they are solids in the pure state at ambient temperature and are not usually thought of in terms of volatility. The PAH with the lowest molecular weight is naphthalene $C_{10}H_8$, which has a melting point of 80 °C and a boiling point of 218 °C. The PAH with perhaps the longest standing reputation for toxicity, as a carcinogen, is benzo(a)pyrene.

All of the above types of compounds were included in the analysis of flue gas streams at the inlet of the hot-side ESP and the outlet of the cold-side ESP. Those elements that are by their nature indestructible in the process of coal combustion were also determined in other materials (coal, feed water, pyrite, bottom ash, and ESP hopper ash). Stream flow rates and element concentrations were used in the calculation of material balances, which were of interest for two reasons: 1) revealing how the input elements, mainly in the coal, are distributed in effluent streams and 2) providing an evaluation of the internal consistency of the analytical data.

Measurements necessary for computing material balances included the flow rates of flue gas and the concentrations of fly ash at the inlet and outlet of the ESP system. These data revealed that approximately 99.5% of the inlet mass of fly ash was removed by precipitation and almost all of the removal of ash occurred in the hot-side ESP.

The sampling of gas streams for air toxics in the above categories was performed mostly by the use of sampling trains based on EPA's Method 5 concept (the VOST was the one exception). That is, flue gas is extracted through a heated probe to a filter in an oven outside the duct, and then after undergoing filtration the flue gas is scrubbed in aqueous impinger solutions where fine particulate matter or selected gaseous matter that passes through the filter is collected. Depending upon the type of compounds to be collected, the sampling train may have to be used in a traversing mode, or it may be used at a single point. Again depending upon the type of compounds of concern, both particulate matter on the filter and substances in the impingers may have to be analyzed, or only the contents of the filter may require analysis.

For the primary categories of the pollutants investigated, the key findings were as follows:

Trace elements

- In the coal, the concentrations of the elements listed above as trace elements occurred at concentrations ranging from approximately 1 μg/g (for beryllium) to 50 μg/g (for vanadium). The overall composition of the coal was such that if combustion caused all of the trace elements to be entrained in the flue gas the concentration of each element in the gas stream expressed in the units μg/Nm^3 would be approximately 100 times the concentration in the coal in the units μg/g. Thus, the maximum calculated concentrations in the flue gas would range approximately from 110 μg/Nm^3 to 5500 μg/Nm^3. (The specific conditions to which these concentrations apply is gas containing 4% O_2 in the dry state at a pressure of 1 atm and a temperature of 68 °F.) This O_2 concentration was selected as the reference concentration because it approximates the actual concentration at the hot-side ESP inlet.

- In the flue gas at the ESP inlet, the measured concentrations departed from the calculated values cited above mainly because of partitioning between the particulate and gas phases. Only two of the elements were primarily in the vapor state; these were mercury and selenium. This conclusion is an inference based upon analyses of various materials: bottom ash, economizer ash, and ash removed from entrainment in the flue gas. It should be understood that the Method 5 filter when operated at 250 °F as stipulated cannot in principle tell the difference between an element in the particulate state and in the gas phase at the inlet duct temperature of 700 °F. By and large, the elements other than the two named were not markedly partitioned between solids in various locations, as between bottom ash and fly ash, for example. It should also be understood that general conclusions as to the disposition of the individual elements, have been very difficult to make in view of the quite considerable uncertainties in the analytical data.

- Whereas the fractional penetration of the ESP system (primarily the hot-side unit being effective) is about 0.5%, the penetrations of the trace elements range roughly from a minimum of 1% for manganese (or others) to 100% for mercury. (This value for mercury, although not perfectly supported by the analytical data, is at least nominally correct.) For the majority of the trace elements that appear to reside primarily as particulate matter, the range of penetrations was roughly from 1 to 5%. There is, therefore, reason to think that these trace elements must have been present mainly as particulate matter in the fine particle size range if they failed to undergo removal by precipitation to the same degree as the overall fly ash mass.

- Calculation of material balance for the trace elements was constrained by the absence of flow rates on some of the streams that in principle must be taken into account. The efforts to construct material balance dealt with two sections of the power plant — 1) the inlet and outlet streams up to the inlet of the hot-side ESP and 2) the inlet and outlet streams at the ESP system and the ash removed in the hot-side ESP. Recoveries of input elements in the gas stream were estimated to have a norm of about 80%, allowing for disposition in the bottom ash and ignoring selective occurrence in the vapor state. Actual calculated recoveries ranged from roughly 15% to over 200%. These values represent extremes in individual tests and may be explained by additive positive and negative errors for the gas stream and the coal. Based on analysis by inductively coupled argon plasma emission spectroscopy (ICP), approximately one-third of the elements were recovered within the range of 60-100%, which is about as narrow a range as can be expected. The results for mercury, when based on sorption tube sampling, were within this range, these results seem to be a striking success compared with the results reported for mercury in other prior investigations. Based on neutron activation analysis instead of ICP, recoveries were somewhat better. Closure of material balance was more successful across the ESP than across that part of the system up to the ESP. At the ESP, the deposition in the hopper ash of the hot-side ESP was compared with the loss from the gas stream. The closure figures at the ESP ranged from 60 to 130% (there were also indeterminate values resulting from individual concentrations assigned only a lower limit).

Acid gases

- The recovery of coal sulfur as SO_2 was approximately 80-90%, a satisfactory range that allows for an indeterminate rejection of sulfur in pyrite waste. The recovery of coal halogens as HF and HCl varied considerably but was consistent with essentially 100% occurring as these compounds at the outlet from the ESPs.

- The emission of nitrogen in the reduced states represented by HCN and ammonia was almost not measurable and not increased by low-NO_x firing.

Aldehydes and ketones

- One compound of each type, formaldehyde and acetone, was measured during the low-NO_x firing; no information for baseline firing was obtained because of errors of judgement in the analysis of the samples. The concentrations of both compounds in the low-NO_x mode were in the range 1-100 $\mu g/Nm^3$.

Volatile organic compounds

- Benzene appeared to occur at highly variable concentrations. Some samples seemed to contain no benzene, implying that the concentration in the duct was as low as 1 $\mu g/Nm^3$; others indicated that the concentrations were as high as 10,000 $\mu g/Nm^3$. Toluene was often detected but at concentrations one to two orders of magnitude below those of benzene. There is no objective basis for discrediting the data on these two compounds, but there is the suspicion that the amounts found were due to artifacts, such as degradation of the polymeric sampling medium Tenax.

- Benzene and toluene represent only a part of the entire spectrum of volatile compounds detected. Many of the other compounds evident from the gas chromatograms and associated mass spectra were not identified; nevertheless, they may represent significant emissions.

- Low-NO_x firing paradoxically did not seem to increase the emission of volatile organics but may even have had the opposite effect. Unfortunately, this statement may be more of a commentary on the uncertainties of sampling and analysis than on the true change in character of the emissions.

Semi-volatile organic compounds

- Naphthalene was the only PAH compound on the target list that was positively identified. Its concentration was approximately at the detection limit, around 2 $\mu g/Nm^3$. (Note: the contrast between the apparent concentration of naphthalene and the highest concentration of benzene cited above is correctly indicated — that is, the concentration of naphthalene is approximately four orders of magnitude lower.)

- The compounds phenol and benzoic acid (the latter is not on the list of toxic chemicals in the Clean Air Act Amendments of 1990) were consistently observed. The concentrations of these two compounds were as high as 500 $\mu g/Nm^3$.

- Low-NO_x firing gave evidence of markedly increasing the emission of semi-volatile compounds, most of which, unfortunately, were not identified.

In the second paragraph of this summary, three questions of primary interest were stated. Some of results presented subsequently bear on these questions. In addition, a concise summary of the answers to those questions is presented below:

1) Effect of low-NO_x firing. There was no clear-cut effect on the emission of trace metals or acid gases. The data give marginal evidence for a decreased emission of Cr(VI), which would be a favorable change but is not certain by any means. The

effect on aldehydes and ketones cannot be stated because of the loss of samples for baseline conditions; no credible data on these compounds were obtained for baseline conditions. The change in volatile organics appeared to be a reduction in emissions, whereas that for semi-volatiles seemed to be an increase. Inasmuch as low-NO_x firing is sometimes accompanied by large increases in the amount of unburned carbon in the ash, the result for semi-volatiles is more in line with expectation.

2) Effect of the hot-side ESP. As indicated above, the hot-side ESP lowered trace-element emissions to the range roughly from 1 to 5% of the levels found in the inlet gas stream. Not surprisingly, the hot-side ESP had no measurable influence on the emissions of SO_x, HF, and HCl. Quite surprisingly, on the other hand, the ESP seemed to suppress the emission of certain organic substances. Suppression of the emission of formaldehyde is particularly difficult to explain. Presumably, the apparent disappearance of organics in the vapor state may be due in part to chemical changes at the high temperature of the ESP or in the corona regions, where ozone and other high-energy reactants are present. Perhaps chemical destruction was aided in the instance of semi-volatile compounds by relatively long residence times at high temperature while the compounds were adsorbed on ash particles in the hoppers.

3) Effect of the cold-side ESP. Limited data with the cold-side ESP in operation made it difficult to detect any but the most emphatic effect of that ESP. No dramatic effect was seen. Little effect, if any, occurred in the control of total particulate matter. The main place, then, to search for reduced emissions would be for materials that are volatile at the hot-side temperature but not volatile at the cold-side ESP. Such materials are mercury and selenium. Improved control of these trace elements was not observed.

The contents of the body of this report can be easily located from the section titles given in the table of contents. Certain important reference material is given in the appendixes, specifically:

- Graphs showing data on particle-size distributions

- Copies of the reports submitted by Brooks Rand, Ltd., covering the analysis of samples of mercury collected on solid sorbents.

- Copies of the reports from the University of Missouri-Columbia, dealing with results of neutron activation analyses.

- Discussion of measures used during this project for Quality Assurance/Quality Control.

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Environmental Sciences — Grady B. Nichols,
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Research Director

Analytical and Physical Chemistry — Herbert C. Miller
Vice President in charge

The principal members of the staff with active responsibility for the project were the following:

Principal Investigator
Edward B. Dismukes,
Principal Chemist, Environmental Sciences Department

Sampling Coordinator
Joseph D. McCain,
Senior Staff Physicist, Environmental Sciences Department

Analytical Coordinator
Robert E. Adams
Head, Analytical Chemistry Division, Analytical and Physical
Chemistry Department

David S. Weinberg was responsible for the analysis of organic materials by gas chromatography/mass spectrometry. Kim W. Baughman was in charge of the remaining analyses,

primarily of inorganic samples, until he resigned from the staff of Southern Research in the first half of 1992. Charlotte S. Lyons became responsible for most of this work subsequently.

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MEASUREMENT OF CHEMICAL EMISSIONS UNDER THE INFLUENCE OF LOW-NO$_x$ COMBUSTION MODIFICATIONS

1. INTRODUCTION

1.1 RESEARCH OBJECTIVES

This report presents the results of a research project on the measurement of chemical emissions from a coal-burning electric power station. The research was conducted by Southern Research Institute under contract with the Power Technologies Department of Research and Environmental Affairs of Southern Company Services (SCS). The funds for the research were provided through SCS on a joint basis by the Electric Power Research Institute (EPRI) and the U.S. Department of Energy (DOE) through the Innovative Clean Coal Technology Program. The electric power station that was the site of the chemical emissions study was designated as Site 110 in the list of EPRI's PISCES investigations. The period covered by this project was August 1991 to September 1992. This period covered the entire research effort, from initial planning and preparation through the final sample analyses and data interpretation.

One of the objectives of the proposed research program was to determine how the emission of so-called "air toxics" will be changed by modifying a coal-burning furnace to lower the emission of nitrogen oxides (NO$_x$). Unit 2 of the test site has been modified to lower NO$_x$ emissions through a modification of the combustion conditions; this modification was made as part of the Clean Coal program of the Department of Energy.

A second objective was to generate data on the emission of air toxics to augment the body of data being compiled under a program of the Electric Power Research Institute. This program is known as Power Plant Integrated Systems: Chemical Emission Studies and is referred to as PISCES (1). The EPRI program and a newer program being instituted by DOE will cover a variety of power plant configurations as defined in terms of fuel type, furnace design, and emission control strategies. Site 110 offered two features that made it attractive for study in connection with PISCES. First, it is unusual in that it provides control over the emission of NO$_x$; however, it does so with modified combustion conditions having the potential of producing unwanted increases in emission of toxic organic compounds and conceivably undesirable changes in the emission of inorganic substances. Second, the plant is unusual in controlling emissions of particulate matter through the combination of a hot-side ESP and a cold-side ESP in a tandem arrangement.

The final objective was to determine whether the cold-side ESP contributes materially to the removal of particulate matter or hazardous air pollutants. The primary removal of fly ash was known to occur in the hot-side ESP; the degree of removal of other material, which might be favored at a lower gas temperature, could only have been inferred. A single day of operation with the cold-side unit energized and three days of operation with the cold-side unit deenergized during each test series were the operational parameters to evaluate the cold-side ESP contribution.

A key approach in the evaluation of the data from this project was to conduct material balances for the overall plant and for the ESP system in terms of those substances whose masses must be conserved throughout all processes occurring. Primarily those substances were trace metals; however, they also included the non-metallic elements sulfur, phosphorus, chlorine, and fluorine.

1.2 TECHNICAL BACKGROUND

Air toxics is a term designating certain hazardous pollutants that are addressed by the 1990 amendments to the Clean Air Act by the U.S. Congress. Title III of the 1990 legislation establishes a list of 189 toxic chemicals whose effects are to be evaluated and regulated as determined necessary by the Environmental Protection Agency.

Regulating air toxics is to occur in two phases (2). During the first phase, within a year, the EPA was required publish a list of source categories emitting 10 tons annually of any one toxic or 25 tons annually of a combination of toxics. The agency subsequently had to issue Maximum Achievable Control Technology (MACT) standards based on the best demonstrated control technology or practices in the industry to be regulated. Within two years, EPA was required to issue MACT standards for 40 source categories and set in motion plans to ensure that all controls will be adhered to within 10 years. The second phase of regulation will take effect

8 years after the first-phase MACT standards. Standards based on health risks will be set in place if a facility's emissions present a cancer risk of more than one per million.

Approximately 90% of the hazardous substances listed in the 1990 act are specific organic compounds, which are made up of the elements carbon, hydrogen, oxygen, nitrogen, and chlorine or another halogen. Most of the remainder of the hazardous elements listed are described more generally as compounds of specific metallic elements: antimony, arsenic, beryllium, cadmium, chromium, cobalt, lead, manganese, mercury, nickel, and selenium. Most of the compounds of these metals are likely to occur as inorganic compounds, specifically including the oxides. Some, however, may occur in organic compounds; mercury is one such example.

Other potentially hazardous pollutants are acidic inorganic gases derived from certain key nonmetallic elements. These include hydrogen fluoride (HF), hydrogen chloride (HCl), sulfur oxides (SO_x), and phosphorus pentoxide (P_2O_5, possibly occurring as phosphoric acid, H_3PO_4).

There is not now available a sampling and analytical protocol that would cover all of the compounds listed in the 1990 Clean Air amendments. There are, however, procedures generally recognized to be appropriate for selected representatives of the classes of compounds that are of concern, including specific compounds from the 1990 act. These procedures are largely based upon analytical developments by the EPA. The plans for the analytical work at Site 110 were based on the EPA-sanctioned methodology, which has been used extensively in previous PISCES studies, as well at Southern Research Institute, in work for the U.S. Army in the disposal of obsolete chemical agents.

In general terms, the objectives at Site 110 were to collect and measure the following:

- Compounds of any form containing the toxic trace metals cited in Table III of the Clean Air Act Amendments of 1990: antimony, arsenic, beryllium, cadmium, cobalt, chromium, lead, manganese, mercury, nickel, selenium. Selenium, for example, occurs in coals typically in the concentration range 1-10 ppm by weight (3), and will be found in the combustion gases in the concentration 100-1000 $\mu g/Nm^3$. (Four other metals which were also evaluated — barium, copper, molybdenum, and vanadium — are not cited specifically as trace components of pollutant emissions by the 1990 Clean Air legislation, but they will occur at trace levels in the pollutants emitted by coal-burning power stations.

- Acidic inorganic gases based on the nonmetals fluorine, chlorine, sulfur, and phosphorus (HF, HCl, SO_2 and SO_3, and P_2O_5 or H_3PO_4)

- Volatile organic compounds, including benzene, toluene, and formaldehyde

- Semivolatile organic compounds, primarily polycyclic aromatics

Further objectives only incidentally related to the occurrence of air toxics were to determine the total concentrations and particle-size distributions of the suspended particulate matter at the inlet and outlet of the dual ESPs.

2. DESCRIPTION OF THE TEST SITE

2.1 GENERAL FEATURES

There are two units at the test site. Unit 1 is rated at 175 MW and Unit 2 at 196 MW. Both units have Combustion Engineering tangentially-fired boilers. Originally, both units were equipped with cold-side ESPs; in 1977, however, when the units were converted to balanced draft operation, both units were also retrofitted with hot-side ESPs. Both units continue to operate with a hot-side and a cold-side ESP in tandem. Flue gas evolved from the two cold-side ESPs is vented to the atmosphere through a common stack.

Over the years, the fuel supply at the test site has varied. About 10 years ago, for example, a low-sulfur coal from South Africa was employed (4). During the past year or longer, on the other hand, coals from Southern Illinois and Western Kentucky containing about 3% sulfur have been used as the fuel. Western Kentucky coal purchased on the spot market, with about 3% sulfur, was burned during both of the test occasions described in this report. As will be shown subsequently, the results of analyses of coal samples from both occasions showed a high level of agreement; thus, differences in the coal were not likely causes of any large differences in the test results. There is no provision at the test site for the removal of sulfur from the flue gas in a scrubber of any type; however, a portion of the sulfur present in the coal as pyrite is removed during the pulverization process prior to combustion and is discharged as a waste stream.

During the first half of 1991, the furnace of Unit 2 began to undergo modification with the installation of burners to produce lower concentrations of NO_x. This report discusses the measurement of emission rates of toxic organic and inorganic substances in the flue gas both before and after the burner modifications were made. The baseline measurements prior to the final adoption of modified combustion conditions were conducted during the period September 17-22, 1991; however, as will be described in the next paragraph, the baseline study was performed after certain structural changes in the furnace had been completed. The subsequent measurements with burner modifications in place were made during the period January 14-17, 1992.

The furnace modification installed at Site 110 to achieve low-NO_x combustion is known as the Low-NO_x Concentric Firing System Level III (LNCFS III) of ABB Combustion Engineering. Figure 1 is a diagram provided by SCS to show the configuration of firing systems in place at Site 110 before the combustion modifications were started, while the modifications were being made, and after all changes had been completed. The configuration in place during the measurements in September 1991 was that designated as LNCFS Level II; to approximate the combustion conditions under the baseline configuration during September 1991, the dampers for overfire air were closed and the nozzles for offset air were set to inject this air in the same pattern as the regular air. The configuration operated for low-NO_x production in January 1992 is the one identified in the figure as LNCFS Level III. The quantitative effect of the furnace modifications on NO_x production is illustrated in detail by data from continuous emission monitors that are presented later in this report.

2.2 INLET AND OUTLET STREAMS

The features of the test site that determined where sampling for pollutants was to be performed are illustrated schematically in Figure 2. The streams that had to be sampled for the purposes of establishing emission rates and closing material balances for the inorganics are also indicated in this figure.

Streams entering the system are these:

- The coal

- The water admitted to the bottom of the furnace to serve as a boiler seal and to transport the bottom ash to the ash pond

The water stream cited above comes from a fresh-water well. There is also a stream of water entering the plant not shown in the figure; this is water from the ash pond that is recirculated as needed for transporting ash to the ash pond. None of the materials sampled and analyzed in this project was affected by the recycled pond water. Care was taken to collect all solids before the materials made contact with the pond water. The bottom ash, however, was necessarily collected after it had been wet with the fresh water.

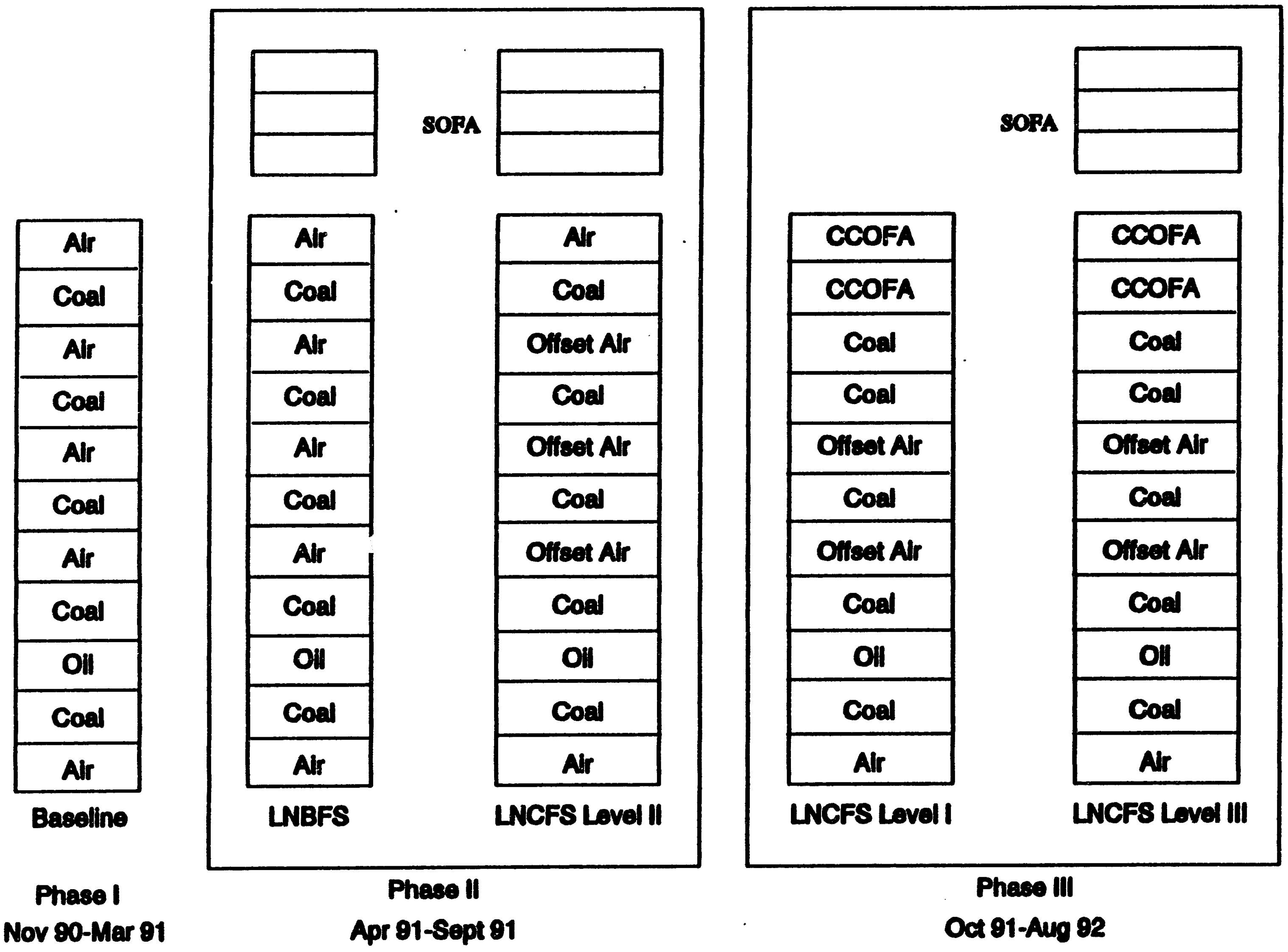


Figure 1. Innovative Clean Coal Technology Demonstration — ABB CE low NO_x concentric firing systems (Figure: courtesy of Southern Company Services, Research and Environmental Affairs).

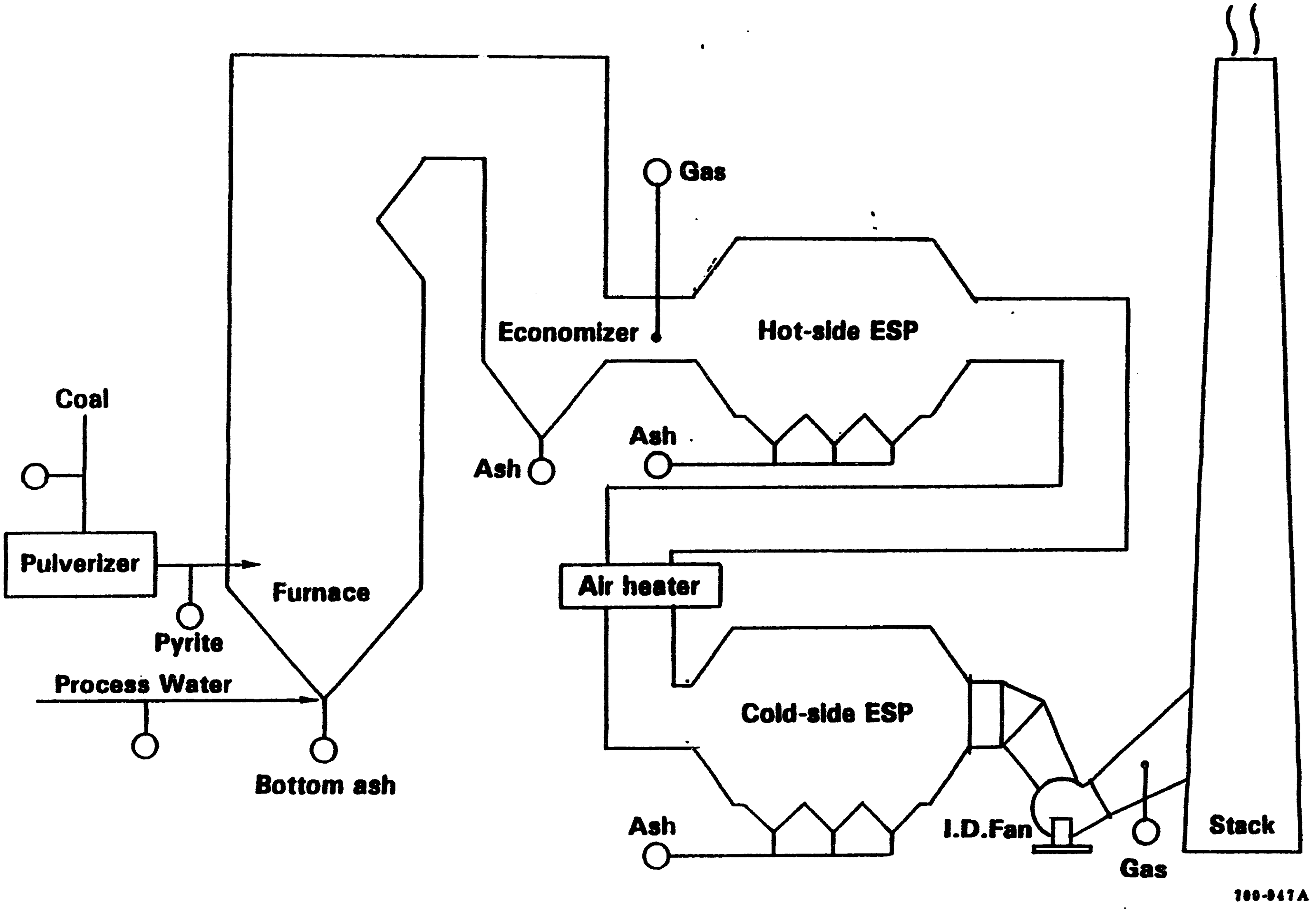


Figure 2. Layout of sampling locations at Site 110.

Streams leaving the system are the following:

- Pyrite waste from the coal
- Bottom ash from the furnace
- Part of the fresh water that is used for sluicing the bottom ash
- Fly ash from the economizer
- Fly ash from the two ESPs
- Flue gas that exits the cold-side ESP and enters the atmosphere through the stack

2.3 SAMPLING LOCATIONS

The coal was sampled after it had been crushed but before it was pulverized and thus, before the pyrite was removed. Samples were collected as the coal was discharged from each of the mills. Approximately 1 pint was collected from each discharge stream at hourly intervals each test day. At the end of the day, the samples were combined, riffled, and divided into different portions, one of which was provided for analysis on this project. All of the work to acquire the coal samples was accomplished by employees of the plant.

The pyrite from the crushed coal was rejected into hoppers that were a part of each coal mill. Each hopper was equipped with a hinged door and a grate at the bottom, where the pyrite was deposited. Employees of the plant inspected the grates once per shift and removed a sample if pyrite was present. At times, no pyrite was found, because there was relatively little pyrite to be removed from the coal being used as a fuel during the time this project was being conducted.

The bottom ash was sampled after it had been collected and transported in water. This material, unlike any of the other solids, was collected in wet form; it could not be collected otherwise.

Samples of fly ash were collected from the hoppers underneath the economizer and the hoppers beneath the hot-side ESP. The original plan was to collect ash from the hoppers of the cold-side ESP as well; this, however, proved to be impossible because the hoppers were always found to be empty when opened. Presumably, the absence of ash in the cold-side hoppers was due to the small amount of ash collected in the cold-side ESP and due also to the draft of air that swept through the hoppers, under negative pressure, when the sampling ports were opened. Removal of ash from the outlet row of hoppers of the hot-side ESP also proved to be impossible. The rate of ash accumulation in the outlet field occurred relatively slowly, and the draft of air that swept through the hoppers when the sampling ports were opened, as with the hoppers of the cold-side ESP, removed the limited amount that accumulated.

The array of hoppers under the hot-side ESP consists of three rows with eight hoppers in each row, as depicted in Figure 3. The hoppers are numbered 1-8 in the inlet row, 9-16 in the middle row, and 17-24 in the outlet row. The ash was necessarily collected from those hoppers that were fitted with sampling ports; the ash was removed specifically from Hoppers 2 and 6 in the inlet row and Hoppers 10 and 16 in the middle row. This ash was analyzed as a suitably weighted composite from the different rows in an effort to construct a material balance of trace elements across the ESPs.

The gas stream entering the hot-side ESP was sampled through three different arrays of sampling ports, as depicted in Figure 4. One set of ports required vertically oriented sampling probes; these ports were located on the roof of the duct that directs flue gas from the outlet of the economizer to the hot-side ESP. These ports are normally operated with connections to thermocouples and gas monitoring equipment. The normal use of the thermocouple ports was interrupted long enough to permit sampling of the gases SO_2, SO_3, NH_3, and HCN. The other two arrays of sampling ports were located on the inside vertical walls of the two ducts that lead gas into the hot-side ESP through a wye. Each set of ports providing horizontal access consisted of a total of nine ports; they were used for all of the remaining sampling operations at the inlet of the hot-side ESP — collection of samples of metals, mercury, acid gases, the organics (volatiles, semi-volatiles, and aldehydes), and size-segregated fly ash. As far as possible, the location of a given type of train was alternated from one duct to the other on a day-by-day basis.

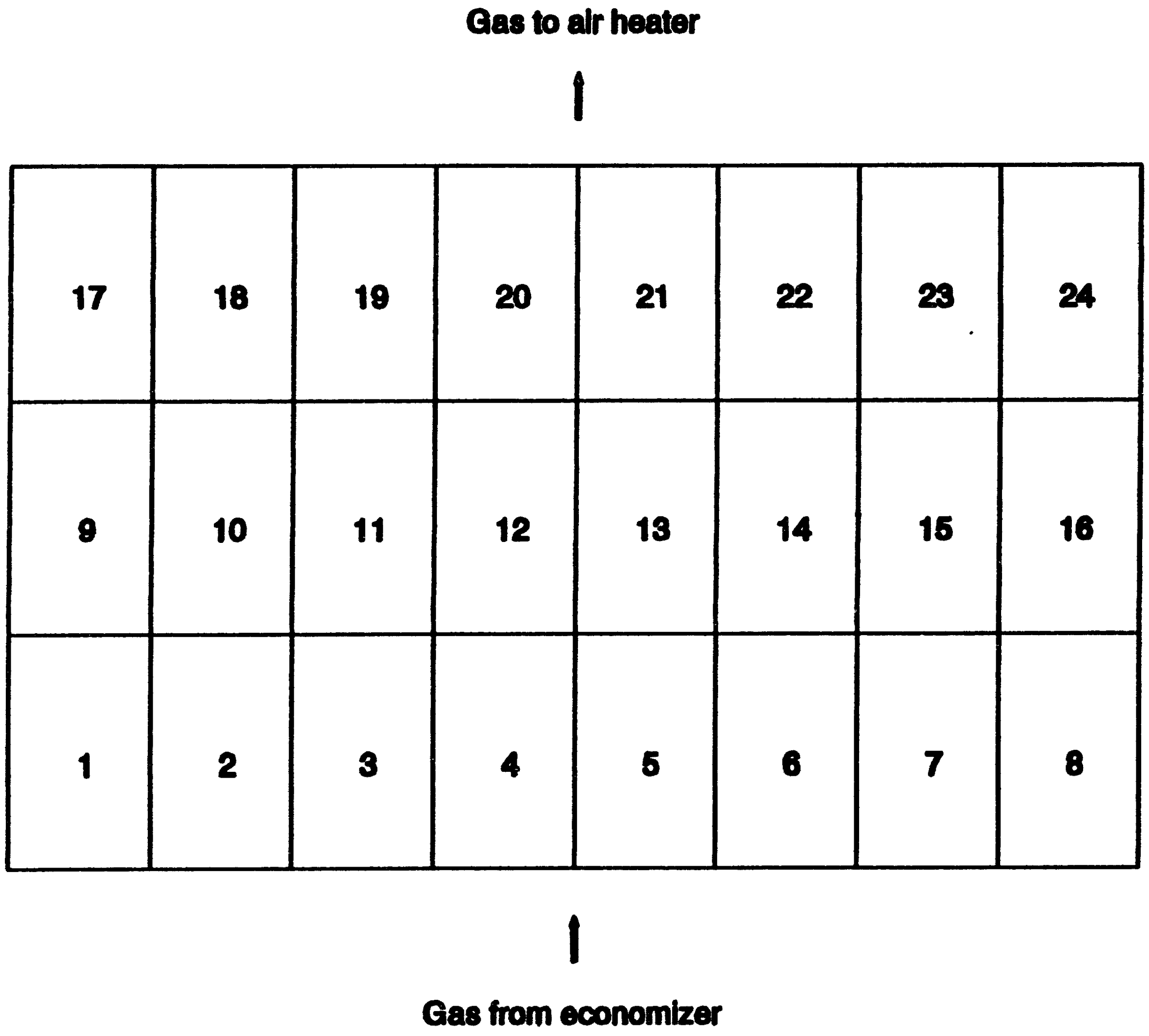


Figure 3. Array of hoppers beneath the hot-side ESP. (Nos. 2, 6, 10, and 16 were those sampled.)

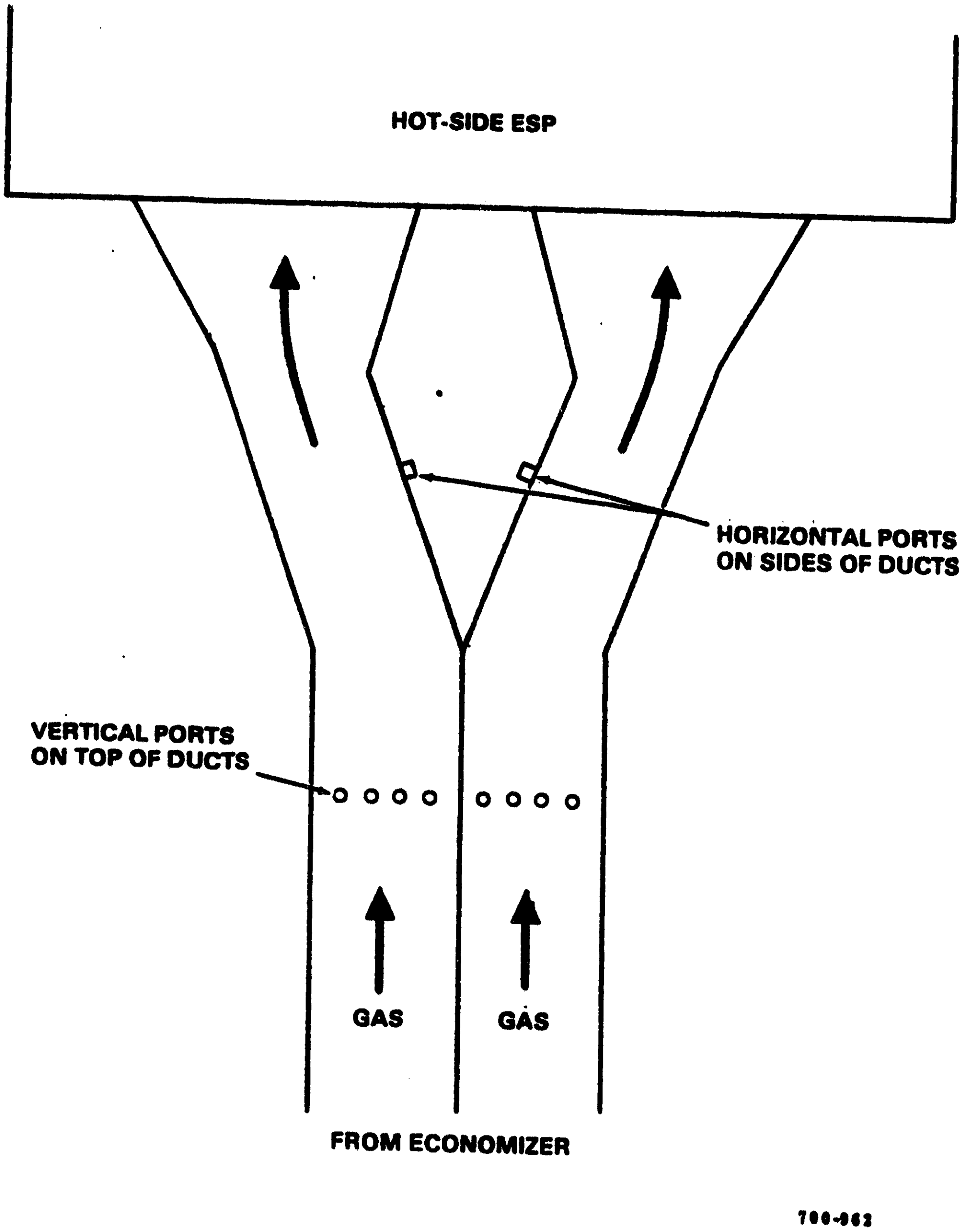


Figure 4. Sampling ports at the inlet of the hot-side ESP.

The gas stream leaving the cold-side ESP was sampled through a series of ports in the outer vertical wall. Near the ESP, there were six ports in a vertical row, which were used for the bulk of the sampling (corresponding to most of the sampling done at the two ducts entering the hot-side ESP). Near the stack, there were two ports side by side that were used for sampling SO_2, SO_3, NH_3, HCN, and mercury. All of the ports between the cold-side ESP and the stacks were between the ID fans and the stack and thus were under positive pressure.

2.4 MATERIAL FLOW RATES

Flow rates of the coal were provided from the computer records of the plant. The rates were recorded for each of five mills at 10-min intervals throughout each 24-hour period. The daily averages presented later in Table 1 of this report were calculated for the hours 0600-2400 for the test days in September and for the hours 0600-2100 for the period in January. These periods covered the entire periods of sampling on each occasion.

Flow rates of only two other streams among those required, in principle, for use in material balance calculations could be evaluated. These were the flow rates of flue gas at the inlet of the hot-side ESP and the outlet of the cold-side ESP. These flue gas flow rates were measured by Pitot traverses of the pertinent gas ducts. The results of the measurements are presented subsequently in Section 4; the flow rates were in reasonable agreement with the rates calculated from the compositions of the coal and the firing rates. Corresponding flow rates of fly ash entrained in the flue gas were calculated as the products of gas flow rate and ash concentration, determined from the weights of ash collected with the out-of-stack filter that was used in the Multiple Metals Train for collecting ash for metals analysis.

The flow rates of the other streams required, in principle, for material balance calculations could not actually be measured and were not recorded with plant equipment. These streams for which flow-rate data were lacking are enumerated below; the consequences of not having the data are also discussed.

- Water for producing the boiler seal and for sluicing the bottom ash. In a strict sense, only the water vapor and the foreign components of the water that evaporate from the boiler seal contributed materials to the part of the system reserved for material balance considerations. Organic compounds in the water were the most likely components of the water to evaporate and become a part of the combustion gas leaving the boiler; these compounds, however, were irrelevant in the sense that no material balance with respect to organics was attempted (the potential for combustion of organic compounds in the coal made a material balance for organics essentially impossible). Substances from the water that were combined with the bottom ash were relevant only in the sense that they became analytically a part of the bottom ash (they remained with the ash when the ash was dried in preparation for analysis).

- Pyrite rejected from the coal feed between the crushers and pulverizers. Sometimes none of this material was available for collection, and when the material was present it included extraneous magnetic waste such as bolts and nuts. Not surprisingly, the analysis of the pyrite samples gave highly variable results, as described later in Section 5.1. Clearly, high relative quantities of coal were rejected along with pyrite (formally, the compound FeS_2). It is thus clear that, even if the mass flow rate of pyrite were known, much repetitive sampling and analysis would have been required to obtain a meaningful input to material balance calculations.

- Bottom ash. Typically, for boilers that fire pulverized coal, 20% or so of the coal ash will appear in the bottom ash. Our data on recoveries of fly ash at the inlet of the hot-side ESP (discussed in Section 4) indicate that this is a reasonable approximation. Moreover, the absence of marked peculiarities in the metals composition of the bottom ash, as described in Section 5.3, lessens the errors that might arise from knowing the rate of accumulation of bottom ash.

- Economizer ash. No information at all about the rate of accumulation of ash in the economizer hoppers was obtainable. The ability to perform material balance calculations in the absence of this information is based on the same logic as mentioned above for bottom ash; the matter is discussed further in Section 6.

- ESP hopper ash. No independent measure of the rate of ash collection and removal in the hot-side ESP was obtained. Similarly, no corresponding measure for the rate in the cold-side ESP was obtained either; however, this latter factor is believed to be small enough to be immaterial (a reasonable deduction based on total ash removals with and without the cold-side unit operating, for which data are given in Section 4). Any information on the accumulation rate and removal rate for the ESP system has to be based on total inlet and outlet ash flow rates in the flue gas.

3. DESCRIPTION OF SAMPLING AND MEASUREMENT PROCEDURES

3.1 SAMPLING TRAINS FOR GAS STREAMS

The strategy of the project with respect to sampling the gas streams was to collect the entire set each day of testing at each location (ESP inlet and outlet). In practice, during the baseline testing series, some adjustments in this plan became necessary, as discussed in Section 3.4.

Several Method 5-types of trains were employed. They were identical with respect to the probe and filtration unit but differed in the contents of the impingers behind the filter. Each probe was 12 ft long and had a heat-traced Pyrex lining; the nozzles attachable to the flue-gas end of the probe were interchangeable and were selected to permit isokinetic sampling. The filter was a 3- or 4-inch quartz-fiber disc that was maintained in an oven at 250 °F. A heat-traced Teflon umbilical 15 ft in length was used to connect the filter compartment within the oven to the impingers, which were kept in a fixed location. An umbilical of this length was necessary to permit full traversing of the duct while the impingers were kept in a fixed location. The solutions used in the impingers to catch vapors or fine particles that penetrated the filters were selected according to the type of material being collected, as described below.

One type of train of the Method 5 type was the Multiple Metals Train, which is illustrated in Figure 5. The procedure for using this train will presumably be incorporated in the next edition of EPA's analysis manual for solid wastes, SW-846, now in the 1986 edition (5). The method is also scheduled to appear in a future edition of 40 CFR as Method 29. This train is presently described in an existing EPA report (6).

The impingers of the Multiple Metals Train include two in series that contain a mixture of H_2O_2 and HNO_3 and two additional impingers in series downstream that contain a mixture of $KMnO_4$ and H_2SO_4. The probe wash and the filter catch are digested and used for determinations of all of the metals of interest. The H_2O_2/HNO_3 impingers are analyzed for all of these same metals in addition. The $KMnO_4/H_2SO_4$ impingers, on the other hand, are analyzed only for mercury. All of the metals except mercury are presumed to be partitioned between solids

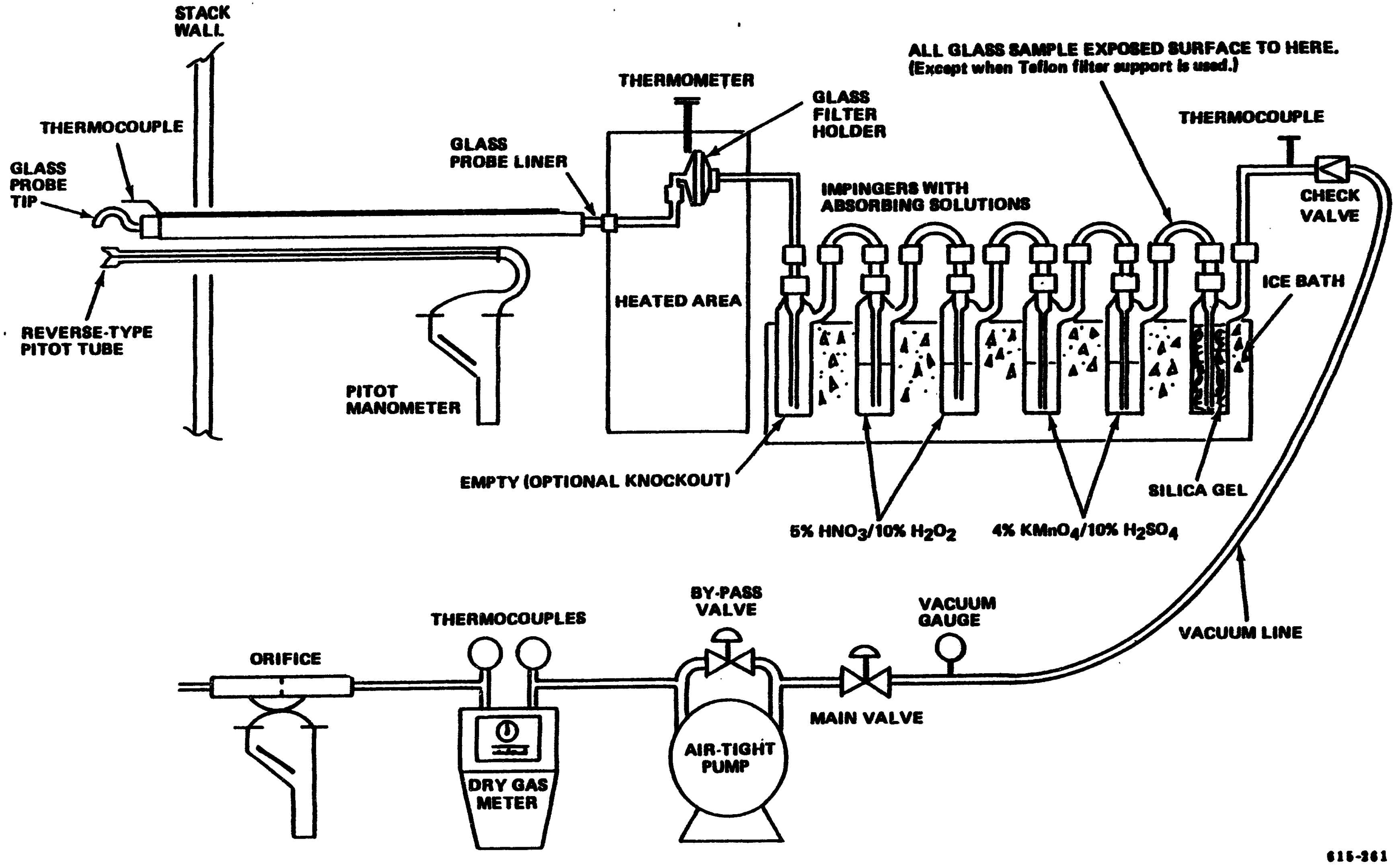


Figure 5. Multiple Metals Train.

retained in the probe and on the filter, plus the H_2O_2/HNO_3 impingers. Mercury is presumed to be in these locations, plus the $KMNO_4/H_2SO_4$ impingers as well.

Another train of the Method 5 type is the so-called Modified Method 5 train, which is illustrated in Figure 6. This train is described as Method 0010 in SW-846. It is used for sampling semi-volatile organic compounds. A cartridge of XAD-2 resin is located behind the filter for collecting vapors from the gas phase. Impingers filled with water are located behind the XAD cartridge to collect vapors that penetrate the solid sorbent.

The third train of the Method 5 type was used for collecting acid gases (specifically HF, HCl, P_2O_5 or H_3PO_4, and SO_2 and SO_3). The Acid Gases Train was described by the Radian Corporation in a guide to sampling and analysis of air toxics of concern to the PISCES program (7). The train employs a heated particulate filter in the customary Method 5 mode, but it depends upon impingers behind the filter to collect only the gaseous compounds of interest. The impingers use a basic solution containing sodium carbonate and bicarbonate with hydrogen peroxide added to trap and oxidize SO_2 to sulfate.

The fourth train of the Method 5 type was used for collecting aldehydes and ketones. This train was also described in the Radian analytical plan cited above. This train differs from the one for formaldehyde that is described in Section 3.6 of EPA/530-SW-91-010 (5), which does not include a filter of the Method 5 type and which collects particulate matter to be analyzed in addition to the vapors caught in the impingers. The Aldehyde Train (more broadly identified as the Aldehyde-Ketone Train) employs impingers containing 2,4-dinitrophenylhydrazine (DNPH) for trapping carbonyl compounds in non-volatile forms, as 2,4-dinitrophenylhydrazones.

A substantially different train from the Method 5 types known as VOST (Volatile Organics Sampling Train) was used for collecting volatile organic compounds; the train is illustrated in Figure 7 and is described in SW-846 as Method 0030. A filter of quartz wool is used in the probe to screen out most of the particulate matter entrained in the gas stream being sampled. There are two sorbent tubes for collecting the vapors. One is filled with Tenax resin, and the second is packed at the front end with Tenax and at the rear end with charcoal. Each sorbent tube is bathed with condensate from the gas stream; the two condensates are analyzed as

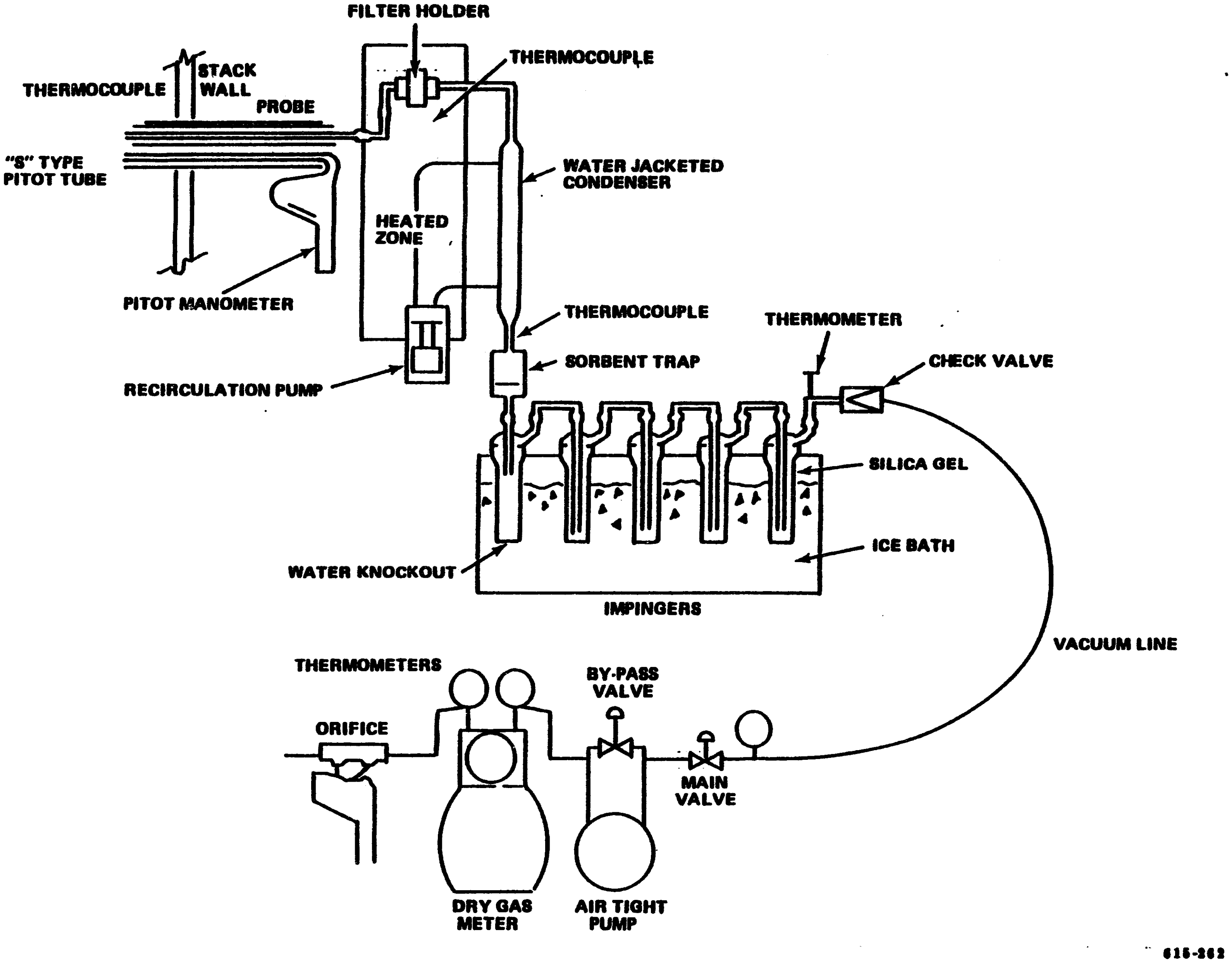


Figure 6. EPA Modified Method 5 Train (MM5).

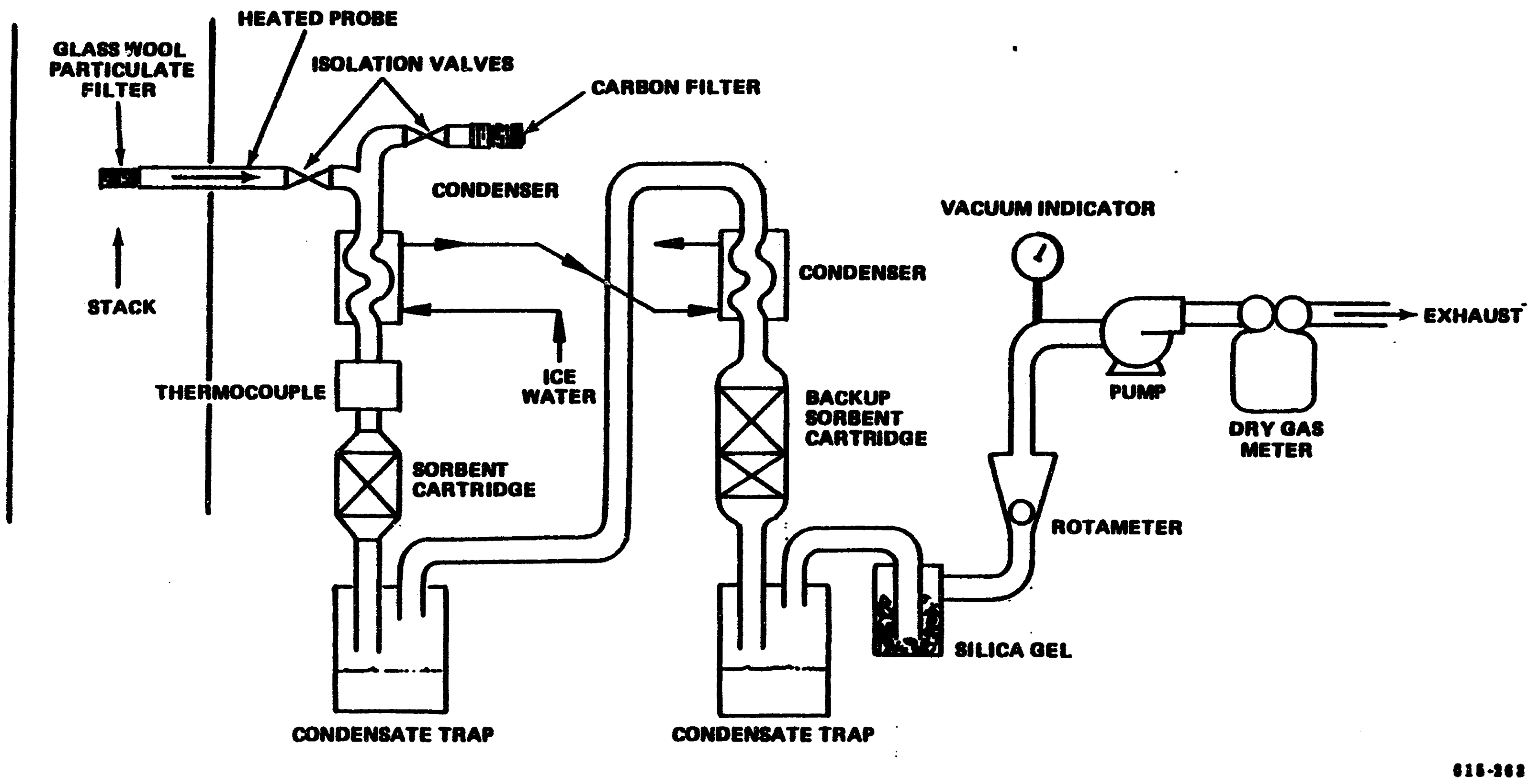


Figure 7. Volatile Organics Sampling Train (VOST).

a composite. The sorbents are subject to being overloaded and suffering from analyte breakthrough during sampling; as a consequence, different pairs of sorbent tubes are used for different sampling times so that at least one pair will not be overloaded and, at the same time, will contain adequate sample for analysis. Sampling times at a gas flow rate of 0.5 L/min were 2, 10, and 40 min during the baseline sampling series; they were 2, 5, and 10 min during the later low-NO_x series. The 40-min samples from the ESP inlet contained too much material to be analyzed and, incidentally, caused significant poisoning of the analytical system.

Other sampling trains for relatively specific analytes are listed below:

- SO_2/SO_3 train (controlled condensation train). This train employs a probe and filter that are maintained near 290 °C, a condenser held at 70 °C, and bubblers containing hydrogen peroxide. The heated probe and filter ensure that the vapor of SO_3 (or, the equivalent vapor of H_2SO_4 that exists at lower temperatures) will be able to reach the condenser but also ensure that particulate matter will be removed from the gas stream. The condenser selectively condenses SO_3 as a binary mixture of H_2SO_4 and water. The bubblers collect SO_2 as sulfate.

- Mercury train. This train was provided and operated by Brooks Rand, Ltd., under the supervision of Nicolas Bloom. It employs four sorption tubes containing solid sorbents – two traps of KCl-treated soda lime and two of iodated carbon. The first two traps collect mercury in the oxidized state (as Hg^{+2} compounds or as organic compounds such as methylmercury – e.g., CH_3HgCl), whereas the latter traps collect elemental mercury vapor. Bloom described this sampling train at a recent conference on air toxics (8).

- Ammonia train. Ammonia was collected in a train normally used for SO_3 but with bubblers containing dilute aqueous sulfuric acid to absorb the gaseous ammonia in place of aqueous peroxide to absorb SO_2. Ammonia is collected in the condenser along with SO_3; part of the condensate is aqueous ammonium sulfate in addition to aqueous H_2SO_4 if SO_3 is in excess of the ammonia.

- Hydrogen cyanide collector. The gas was filtered and then passed through an alkaline solution of sodium carbonate and sodium bicarbonate. During the baseline testing, a separate train was set aside for this purpose. During the low-NO_x testing, to simplify the sampling procedures, peroxide was omitted from the impingers of the Acid Gases Train and HCN was collected in the carbonate/bicarbonate solution along with the other acid gases.

Suspended particulate matter was collected for determination of mass concentration in the front half (probe and filter) of the Multiple Metals Train. It was collected for particle sizing in either of two ways. At the inlet of the hot-side ESP, a series of cyclones were used. At the outlet, University of Washington impactors were employed.

3.2 SAMPLING OF COAL, ASH, AND WATER

The plan for analyzing the solids and the water was, first, to acquire several samples of each during each test day and, then, to make a composite of all samples of a given type for each day and to perform the analysis of the composite. This plan was followed insofar as it proved practicable; however, as indicated in Section 2.3, there were difficulties in obtaining all of the different kinds of materials on a regular basis.

The procedure used to obtain coal samples described previously in Section 2.3 yielded a daily composite; approximately 2 lb of coal from the composite was made available for analysis on this project. The procedures used to obtain the water and other solids were also described in part; the key features of the sampling procedures are reiterated and described more broadly here:

- Pyrite was available to be recovered from the hopper grates only intermittently. This material was not collected every test day.

- Samples of water were taken from a pipe that feeds the bottom water seal of the furnace and the sluicing arrangement for the bottom ash.

- There are four economizer hoppers. The one designated No. 44 was the only one that had a fitting that provided access for sampling. A threaded rod was inserted into the hopper for raking ash out into a scoop. At times there was suction on the opening into the hopper which indicated that the ash depth was not great enough for a sample to be removed. Consequently, samples of economizer ash were not obtained on a regular basis.

- Selected hoppers under each ESP are fitted with sample ports, which consist of 1-in. pipe nipples with gate valves. Each port is located about 18 in. above the bottom of the hopper and about 30 degrees below horizontal. A rod was inserted into the hopper to induce ash to stream out through the port onto the floor. After a time, when the ash streaming out of the hopper was thought to be fresh, part of it was caught in a bucket and, when cooled, was transferred to a sample container.

For all samples, making composites was a straightforward matter of combining the individual samples of a given type. For the ESP hopper ash, the task was more complex. The added complexity arises from the fact that differences occur in the physical properties (especially particle size) and also the chemical properties of ash when collection occurs in different electrical fields and thus in different rows of hoppers. The first step in making a composite for the entire available catch of the ESP was to mix equal amounts of samples from hoppers on the front row and then the same for samples from the middle row. Composites representing the different rows were then mixed on a weighted basis to obtain a composite for both rows. The principle used for weighting was based on the Deutsch relationship for a three-field ESP with equal collecting areas in all three fields:

Total fractional penetration = x^3

where x = mass fraction of ash entering each field that is not collected there.

If the overall mass efficiency is about 99%, as at the test site, the value of the fractional penetration is 0.01; hence, $x = 0.215$. The fractions of the inlet ash that are collected in the three fields is then 0.7846 in the first field, 0.1690 in the second field, and 0.0364 in the third field. Consequently, the composite representing the inlet and middle rows of hoppers was prepared to contain ash from the two sources in the mass ratio 0.7846/0.1690 (there was no ash from the outlet row to include in the composite).

3.3 ANALYTICAL METHODS

3.3.1 Metals

Total concentrations. The primary method used for determining metals was Inductively Coupled Argon Plasma Emission Spectrometry (ICP). The types of samples analyzed for metals by ICP were coal, ash, and impinger solutions from the Multiple Metals Train. The two solids had to be digested with concentrated acids at elevated temperatures to place the metals in solution; the digestion procedure used a combination of concentrated mineral acids in a microwave oven. There is a procedure for digesting the solids that is included in the description of the metals sampling train (6); however, the findings in this project were that this procedure, involving treatment of the solids with a mixture of HNO_3 and HF, would sometimes leave substantial fractions of the solids undissolved. Ultimately, the most satisfactory procedure found consisted of an initial digestion of the solids with a mixture of HNO_3, HF, and HCl, followed by a final digestion with H_3BO_3 added to the remaining mixture of the original three acids. This procedure was adopted from recommendations from CEM Corporation, the manufacturer of the microwave oven used in the digestions.

The method used for carrying out metals analysis by ICP is described in SW-846 as Method 6010. This method lacks sensitivity for some of the metals of interest. Therefore, when the sample quantity was limited and the metal concentration in the solution prepared for analysis was limited, supplemental analyses were performed by auxiliary methods based on Atomic Absorption Spectrometry (AAS), which had greater sensitivity than ICP. The metals analyzed by the supplemental procedures, the forms of AAS used, and the SW-846 methods employed were as follows:

Antimony (Sb)	GFAAS (graphite furnace AAS)	Method 7041
Arsenic (As)	GFAAS	Method 7060
	HGAAS (hydride generation AAS)	Method 7061
Cadmium (Cd)	GFAAS	Method 7131

Chromium (Cr)	GFAAS	Method 7191
Mercury (Hg)	CVAAS (cold vapor AAS)	Method 7470
	AFS (atomic fluorescence)	(Not SW-846)
Lead (Pb)	GFAAS	Method 7421
Selenium (Se)	GFAAS	Method 7740
	HGAAS	Method 7741

For mercury collected in the Multiple Metals Train, CVAAS was the method used in the Southern Research laboratory. For this metal collected alternately on sorption tubes, as will be described subsequently, analysis by the more sensitive method, AFS, was performed by another laboratory, Brooks Rand, working under purchase order.

A second method (apart from ICP and the AAS methods) was used for determining a majority of the metals of interest. This was Instrumental Neutron Activation Analysis (NAA). Selected samples of coal and ash were submitted to the University of Missouri-Columbia, where the irradiation and counting were done in the Research Reactor Facility under the direction of Dr. Michael D. Glascock. Four of the metals could not be determined by NAA, either because irradiation does not yield a suitable radioisotope for counting or because the laboratory lacked the appropriate counting equipment. The metals not included in NAA were Be, Cd, Cu, and Pb. The metals not determined by NAA were determined by flame injection AAS at Southern Research to obtain a complete set of results apart from the data provided by ICP, GFAAS, HGAAS, and CVAAS.

Individual species of selected metals. Certain metals, including arsenic and chromium, have different toxicities in different chemical forms. For mercury, the issue is whether mercury is emitted in oxidized forms that can have effects only at relatively remote locations. Practically speaking, the likelihood of local effects depends upon the occurrence of compounds of Hg(II) and organometallic compounds such as methylmercury. For chromium, the question is how much of the metal occurs in the hexavalent form, CR(VI). For arsenic, the question is the degree of partitioning between the trivalent and pentavalent states, As(III) and As(V).

Speciation of mercury was performed by analysts working under the direction of Nicolas Bloom of Brooks Rand, Ltd., of Seattle, Washington. The relevant sampling train that Bloom has developed (described previously in an earlier part of the discussion of analytical methodology) contains a tandem arrangement of four sorption traps, the first two of KCl-treated soda lime and the second two of iodated carbon. These traps operated in a heat-controlled probe, behind a quartz wool plug for filtration, at a temperature of about 120 °C. Little mercury is collected on the quartz wool as solid matter; most of the mercury is vaporous and undergoes sorption in the traps. The KCl/soda lime traps collect methylmercury and divalent inorganic mercury (probable forms of these species are CH_3HgCl and $HgCl_2$). The iodated carbon traps elemental mercury. The analysis of the traps is complex, as Bloom has recently described at a technical conference (8). The critical step is vaporization of all forms of mercury and measurement by atomic fluorescence, which permits determination of concentrations down to 0.05 $\mu g/Nm^3$ in a gas volume of only 20 L.

Speciation of chromium, specifically the quantification of Cr(VI), was performed by Method 425 of the California Air Resources Board, which is similar to EPA Method 7196 of SW-846. This method determines only Cr(VI) that is water-soluble; it does not provide any step whereby Cr(VI) that is located within the aluminosilicate matrix of individual ash particles may be extracted into the aqueous solution and then quantified. The extracting solution contains 20 g of NaOH and 30 g of Na_2CO_3 in 1.0 L; the Cr(VI) extracted is measured colorimetrically at 540 nm as a complex with diphenylcarbazide.

Both the CARB and EPA method descriptions carry warnings of interference from molybdenum and vanadium if these metals are present at high concentrations. The possibility of interference was investigated during the work with the samples from this project; the results indicated that, even though molybdenum and vanadium could be much more concentrated than Cr(VI) in extracts of the ash, their effects on the measured color could be ignored. The data for one sample of ESP hopper ash illustrate the results obtained in the inquiry about interference; these data are illustrated below:

Total concentrations in the $NaOH/Na_2CO_3$ extract were as follows:

Cr	0.171 μg/mL
Mo	2.19 μg/mL
V	3.77 μg/mL

Apparent concentrations of Cr(VI) with spikes added changed as follows:

Spike added	Apparent Cr(VI) concn, μg/mL
None	0.052
Cr(VI), 0.25 μg/mL	0.253
Mo(VI), 2.00 μg/mL (molybdate)	0.039
V(V), 4.00 μg/mL (vanadate)	0.062

The molybdenum and vanadium, added as ammonium salts in amounts roughly equivalent to the amounts of these metals already present, made far lower colorimetric effects than the spike of Cr(VI); the interference from the molybdenum was slightly negative and that from the vanadium was slightly positive. One can conclude that in the actual extract, without spikes, the two interfering metals produced offsetting effects with an insubstantial combined effect.

There is an alternative method developed by EPA for Cr(VI), in which there is a special sampling train with an alkaline absorbing solution continually sprayed into the inlet to stabilize water-soluble Cr(VI) during sampling (6). One of the deficiencies of the EPA method is that SO_2 may be absorbed in the solution at a concentration sufficiently high to reduce Cr(VI) to Cr(III); because of the high SO_2 concentration in the flue gas at the test site, the EPA method was not appropriate at that location.

Only Cr(VI) data for solid samples are presented in this report. Certain determinations of Cr(VI) were made with peroxide-containing impinger solutions and, surprisingly, the results indicated that Cr(VI) and total chromium could be differentiated, suggesting that not all of the Cr(III) captured was oxidized to Cr(VI). None of the results for the impinger solutions are presented in this report, however, since no effort was made to evaluate the stabilities of the two forms of chromium on a quantitative basis when both are in the peroxide medium.

Determinations of As(III) and As(V) in water-soluble forms were made by the method of Weigert and Sappl (9). Ash samples were extracted with water; to one aliquot HCl was added and to the other citrate buffer was added. Sodium borohydride was next added to convert arsenic to AsH_3, which was measured by HGAAS. With HCl present, total arsenic was determined (usually, this was mostly As(V)); with citrate added instead, only As(III) was measured. Although the extract of a sample must have contained species capable of oxidizing As(III) or reducing As(V) — for example, Cr(VI) as an oxidizing agent or sulfite as a reducing agent — spikes of arsenic were sufficiently stable to be recovered as AsH_3 from either HCl or citrate medium.

3.3.2 Acid Gases and Ammonia

Samples from the acid gases train. The analytes determined from the gases absorbed in the acid gases train were fluoride ion, chloride ion, sulfate ion, and phosphate ion. The sulfate collected in this train presumably came mostly from SO_2 in the gas stream; virtually none of the sulfate was likely to have come from the SO_3 (or H_2SO_4 vapor) in the flue gas because the temperature of the Method 5 filter (250 °F) would not allow more than 2-3 ppm of SO_3 to penetrate. The normal procedure with the sampling train was to include peroxide in the carbonate/bicarbonate buffer to oxidize absorbed SO_2 to sulfate. This procedure was followed in the baseline sampling series. The peroxide was omitted from the carbonate/bicarbonate solution during the low-NO_x series to permit HCN to be captured in a stable form, without the need for a separate train. Despite the omission of peroxide, sulfate rather than sulfite was present at the time of analysis.

Chloride, sulfate, and phosphate were measured by ion chromatography. Fluoride sometimes gave a readable signal by ion chromatography, but it suffered from interference from the carbonate/bicarbonate medium used in the analysis. Fluoride was thus determined for the record by use of an alternative procedure, based upon an ion-selective electrode.

SO_2 and SO_3 (H_2SO_4 vapor). The two portions of sample from the SO_x sampling train were analyzed by ion chromatography. Both SO_2 and SO_3 as collected were determined as sulfate; SO_2 was converted to sulfate during sampling owing to the use of peroxide in the sample collector.

HCN and NH_3. These gases were collected in different trains and were analyzed separately. Both, however, were measured with ion-selective electrodes in alkaline media. In such a medium, HCN exists as cyanide ion and is measured with a cyanide-specific electrode; although collected in an acidic medium as NH_4^+ ion, ammonia is formed in the alkaline medium and measured with an ammonia-selective electrode.

3.3.3 Aldehydes and Ketones

The method described here for determining aldehydes and ketones is the appropriate method and was used correctly for samples from the low-NO_x test series. It was not used properly, however, for samples from the baseline series; as a consequence, no useful result for aldehydes and ketones from the first test series was obtained. The errors that were made with those first samples are described later in Section 5.4.3.

Aldehydes and ketones were determined by a method developed by EPA for samples from the ambient environment. The specific method followed is T0 5 (10). This method is similar to the analytical procedure incorporated in SW-846 Method 0011A (6). The aqueous solution of 2,4-dinitrophenylhydrazine in which the compounds are trapped is extracted with a mixture of methylene chloride and n-hexane; the organic solvent is then removed by evaporation and the dry residue is dissolved in methyl alcohol. The hydrazone derivatives are separated and quantitated by High Performance Liquid Chromatography with an ultraviolet detector.

The sample volumes during the low-NO_x test series averaged about 1.4 Nm^3. The final measurement of the compounds was performed with the compounds in 5 mL of methyl alcohol. The limit of detection expressed for formaldehyde, for example, was about 0.5 μg. Thus, the equivalent limit of detection of formaldehyde in the original flue gas was about 0.4 $\mu g/Nm^3$ or 0.3 ppbv.

3.3.4 Volatile Organic Compounds

Volatile compounds collected from the flue gas duct were determined by SW-846 Methods 5040 and 8240. The first step of the procedure is a so-called "purge and trap" procedure, whereby volatile organics in each of the three sample components of the VOST (water condensate, Tenax tube, and Tenax/charcoal tube) are vaporized and then collected on another sorption tube, which contains several different packing materials. Next, the volatile matter is desorbed thermally from the intermediate sorption tube and conveyed in the vapor state to the gas chromatographic column. The components of the sample are separated on the GC column and detected as they are eluted by mass spectroscopy. The manner in which the MS signal is interpreted is described at length in Section 5.4.4.

3.3.5 Semi-Volatile Organic Compounds

SW-846 Method 0010 describes the preparation for analysis of samples of semi-volatile organics, as well as the sampling train that provides the samples. Sample preparation yields a single extract solution, with methylene as solvent, from the several components of the sampling train. The method allows for reduction of the extract volume by evaporation to the range 1-10 mL. Obviously, the smaller the volume, the greater sensitivity the method provides, unless contaminants offset the advantage of less volume. Extract volumes were 10 mL in the work with baseline samples, where a deep coloration suggested either contamination or an unusually high concentration of sample matter. Extract volumes were reduced to only 1 mL in the low-NO_x test series, and method sensitivity was proportionally increased. The analysis of the extracts by GC/MS, according to SW-846 Method 8270, utilizes the single extract from one sampling experiment. In other words, the analysis of semi-volatiles yields only one chromatogram, whereas the analysis of volatiles yields three or four chromatograms, depending upon whether two separate portions of water condensate are analyzed in place of a composite. The interpretation of the data from the GC/MS analysis is discussed in Section 5.4.5.

3.4 SAMPLING SCHEDULE

Originally, the sampling at Site 110 was intended to provide an evaluation of performance with only the hot-side ESP energized. Later, however, before the project was approved, the operating utility requested that the cold-side ESP be energized for one day of testing on each occasion, during baseline or low-NO_x operation. As events transpired, during the baseline testing in September 1991, the cold-side ESP was operated on three days. The first day of operation with the cold-side unit energized was intended to be a full test day that would provide a full complement of samples. Various difficulties and delays on that occasion, September 17, led to rescheduling of the first day of testing on September 18. Even then, a short period of further operation on September 22 was required to complete sampling with the cold-side ESP energized.

The days of sampling and conditions with respect to ESP operation were as follows:

		ESP operation	
Boiler operating mode	Date	Cold-side	Hot-side
Baseline	Sept. 17	on	on
	Sept. 18	on	on
	Sept. 19	off	on
	Sept. 20	off	on
	Sept. 21	off	on
	Sept. 22	on	on
Low NO_x	Jan. 14	on	on
	Jan. 15	off	on
	Jan. 16	off	on
	Jan. 17	off	on

4. DISCUSSION OF PHYSICAL CHARACTERIZATIONS

4.1 COAL FIRING RATES

The test unit at Site 110 was operated at full load (just under 200 MW) on each day of sampling in both September 1991 and January 1992. Full load was maintained from 0600 to 2400 hours daily on the occasion in September, when sampling sometimes was not completed until late in the evening. Full load was required for shorter times daily in January, when sampling was completed by 2100 hours, or earlier.

The record of unit load and coal feed rate through each of five mills was obtained from a computer record maintained by the plant. The values of both parameters were recorded at 10-min intervals for 24 hours per day and were averaged. The average unit load and average coal feed rate for each test day are listed in Table 1. The value of thermal input rate corresponding to the coal feed rate (based on calorific values of the coal, which are given later in Table 3) and the ratio of electrical power to thermal input rate (efficiency) are also listed in this table. The data indicate that the electrical power output was slightly higher in January than in September although the coal firing rate decreased by a somewhat greater degree. This anomaly can be explained as the result primarily of higher calorific values in January.

4.2 GAS FLOW RATES AND PARTICULATE CONCENTRATIONS

The gas flow rates were determined in the ducts upstream from the hot-side ESP and downstream from the cold-side ESP by traverses with a Pitot. The mass concentrations of suspended particulate matter were determined from data obtained in the operation of the Multiple Metals Train (the procedures for use of this train permit the option of recovering and weighing the collected particulate matter if desired). The concentrations of O_2 were measured with the Teledyne instrument. The results of these measurements are presented in Table 2, which also includes certain other information:

- Gas temperatures at the inlet of the hot-side ESP were approximately 700 °F and at the outlet of the cold-side ESP about 340 °F in the baseline measurements or about 320 °F in the low-NO_x measurements.

Table 1
Electrical Power and Coal Firing Rates

	Electrical power, MW	Coal rate, lb/hr	Thermal power,[a] MW	Apparent efficiency, %
Sept. 18	196.66	166,180	573.09	34.32
19	196.50	168,260	582.58	33.73
20	196.47	168,940	590.83	33.25
21	197.65	169,940	595.52	33.19
Jan. 14	197.59	162,160	572.58	34.51
15	198.62	163,730	577.98	34.36
16	197.64	163,530	577.22	34.24
17	198.05	164,030	581.54	34.06

[a] Calculated as the product of the coal rate and the calorific value given in Table 3, with conversion to the units MW = MJ/s = (Btu x 1054.8)/ (1 x 10^6 x 3600).

Table 2
Flow Rates of Flue Gas and Fly Ash

	September 1991				January 1992			
	9/18	9/19	9/20	9/21	1/14	1/15	1/16	1/17
Measurements								
1) Hot-side ESP inlet								
gas flow rate, m^3/min (actual)	10,776	10,913	11,029	11,069	11,095	10,849	10,421	11,453
ash concentration, g/m^3 (actual)	6.39	7.17	7.40	8.20	8.56	6.82	8.48	6.99
O_2 concentration, %	3.8	4.0	4.1	3.8	4.0	3.8	4.4	3.9
gas temperature, °F	705	709	708	709	684	703	689	705
2) Cold-side ESP outlet								
gas flow rate, m^3/min	13,718	13,873	13,465	14,861	13,615	13,551	14,081	14,174
ash concentration, g/m^3	0.0292	0.0255	0.0350	0.0302	0.0443	0.0635	0.0538	0.0620
O_2 concentration, %	6.2	7.6	8.0	8.8	7.0	7.5	7.5	7.5
gas temperature, °F	347	345	344	342	320	312	311	315
Calculations								
1) Coal yield								
gas flow rate, Nm^3/min (4% O_2)	11,405	11,410	11,358	11,629	11,159	11,269	11,167	11,373
ash flow rate, kg/min	114.3	115.0	116.2	119.8	101.5	99.4	102.3	106.1
ash concentration, g/Nm^3 (4% O_2)	10.02	10.08	10.23	10.08	9.10	8.82	9.06	9.33

Table 2 (Concluded)
Flow Rates of Flue Gas and Fly Ash

	September 1991				January 1992			
	9/18	9/19	9/20	9/21	1/14	1/15	1/16	1/17
2) Hot-side ESP inlet								
gas flow rate, Nm^3/min (4% O_2)	10,914	10,913	10,964	11,199	11,094	10,977	10,174	11,520
ash concentration, g/Nm^3 (4% O_2)	6.32	7.17	7.54	8.10	8.56	6.74	8.68	6.95
gas flow rate, % of calcd	95.6	95.6	96.5	96.3	99.4	97.4	91.1	101.3
ash concentration, % of calcd	63.0	71.2	73.7	80.4	94.1	76.4	95.8	74.5
ash flow rate, % of calcd	60.4	68.0	71.1	77.5	93.6	74.4	86.3	75.5
3) Cold-side ESP outlet								
gas flow rate, Nm^3/min (4% O_2)	11,933	10,917	10,278	10,643	11,198	10,744	11,165	11,239
ash concentration, g/Nm^3 (4% O_2)	0.0336	0.0324	0.0454	0.0422	0.0539	0.0801	0.1038	0.0782
gas flow rate, % of calcd	104.6	95.7	90.5	91.5	100.4	95.4	100.0	98.8
gas flow rate, % of inlet	109.3	100.0	93.7	95.0	100.9	97.9	109.7	97.5
ESP efficiency	99.47	99.55	99.40	99.48	99.37	98.81	98.80	98.87

- Actual gas flow rates and fly ash concentrations adjusted to 4% O_2 approximately the concentration of O_2 at the hot-side ESP inlet. Gas volumes are expressed in the units Nm^3, which are on the dry basis with 68 °F or 20 °C as the reference temperature.

- Expected rates of flue gas flow and values of fly ash concentration (the latter assuming complete entrainment in the flue gas of all the ash in the coal). These data were calculated for 4% O_2 from the coal analyses given later in Table 3.

- Gas flow rates and ash concentrations at the hot-side ESP inlet and gas flow rates at the cold-side ESP outlet as percentages of the expected values based on the coal composition and firing rate.

- Ash recovery at the hot-side ESP inlet, which is the observed mass flow rate (product of observed gas flow rate and ash concentration) as a percentage of the ash production rate, again assumed to be entirely as fly ash.

- ESP collection efficiencies (based on actual ash concentrations, compared at the hot-side ESP inlet and cold-side ESP outlet).

The major observations from the information in Table 2 are as follows:

- Gas flow rates at the hot-side ESP inlet were in the range 91.1-101.3% of the expected values. These rates at the cold-side ESP outlet were 90.5-104.6% of the expected values.

- Ash concentrations at the hot-side ESP inlet were in the range 63.0-80.4% of the maximum possible values based on total coal ash in September or in the range 74.5-95.8% of the maximum possible values in January. A rule of thumb sometimes used to predict fly ash concentrations is that 80% of the coal ash will be found as fly ash in the flue gas and 20% will be found as bottom ash. The observed values bracket the figure of 80%. Other measurements at this plant by personnel of Southern

Research at different occasions in 1991 and 1992 found these percentages of coal ash as fly ash entering the hot-side ESP: 82%, 65%, and 70%.

- Ash recoveries at the hot-side ESP inlet ranged from 60.4 to 93.6% in all eight tests. They were higher in the low-NO_x testing than in the baseline testing. The reason is not apparent; the data from earlier studies just mentioned above show considerable variability as well.

- ESP efficiencies ranged from 99.40 to 99.55% in September or from 98.80 to 99.37% in January. The data suggest that there was a slight degradation of the ESP performance as the consequence of the change in combustion conditions. As for the effect of the cold-side ESP as a contributor to fly-ash control, the data indicate that the effect was small at best in September. The cold-side ESP operated on the 18th but not on the other dates; the efficiency changed from 99.47% on the 18th to an average of 99.48% on the next three days. In January, with the cold-side ESP operating on the 14th, the efficiency was 99.36%; it apparently degraded to an average of 98.99% on the next three days when the cold-side unit did not operate (the penetration increased from 0.64% to an average of 1.01%).

The data in Table 2 do not include results from September 21 when the outlet was sampled during sootblowing of the air heater. At that time, the measured outlet dust concentration was 0.1250 g/Nm^3, in comparison with the value of 0.0522 g/Nm^3 in the table for the same day when sootblowing was not in progress.

4.3 ASH PARTICLE-SIZE DISTRIBUTIONS

Figures given in Appendix A present the results of particle-sizing experiments. At the ESP inlet, sizing was accomplished with five cyclones in series, with a back-up filter for the very finest material. At the outlet, University of Washington Mark V impactors were used. The impactors had seven stages with a back-up filter.

The figures cover both test series, baseline and low-NO_x. Successive figures compare a given parameter as measured first in the baseline test series and then in the low-NO_x series; this arrangement facilitates the comparison of the effects of the different boiler conditions on the individual parameters.

The figures give, for each series, averages and 90% confidence limits for four inlet experiments, one outlet experiment with the cold-side ESP energized, and averages with 90% confidence limits for three experiments with the cold-side ESP deenergized. For each of the measurement conditions, there are two graphs of particle-size parameters as functions of particle size; the first in each pair is for cumulative percent of mass and the second is for the differential mass concentration dM/dlog D. In the plots of cumulative mass, the parameter "probit" is used as the linear parameter on the vertical axis; this parameter was selected because its linearity is useful for plotting purposes. Probit has a complex mathematical derivation but its practical importance is obvious through its relationship to the familiar probability distribution on the righthand vertical axis.

The principal observations from the twelve graphs on particle size are the following:

- The inlet particle-size distributions were virtually identical.

- The outlet distributions with the cold-side ESP energized showed minor differences. The cumulative mass plot was steeper up to 2 μm and flatter above 10 μm for the baseline operating condition. The consequence of this in the differential plot was that the peak was steeper on the side of larger particle sizes.

- The outlet distributions with the cold-side ESP deenergized were very similar in both test series.

- The outlet distributions with the cold-side ESP energized or deenergized were hard to distinguish in either test series.

All of the above statements are consistent with information based on determinations of mass concentration with the Method 5 type train, indicating that the cold-side ESP had very little influence on performance and that the overall performance of the ESPs was nearly the same in each test series, baseline and low-NO_x, or possibly somewhat less in the latter series.

Experience elsewhere on the effect of low-NO_x firing shows that this modification can significantly enhance the amount of unburned carbon in fly ash, especially in coarse particle-size ranges, above 74 μm (200 mesh). Experience at Site 110 has been different, however, there being generally no indication that the carbon content of ash increased after the furnace modifications were made.

5. RESULTS OF CHEMICAL ANALYSES

5.1 COAL AND PYRITE

Composite samples of coal from four dates during each of the two test series (baseline and low-NO_x) were submitted to Commercial Testing and Engineering Company for proximate and ultimate analyses. The results subsequently provided by CT&E are presented in Table 3. The composition of the coal appeared to be highly uniform during each test series, and the compositions did not differ a great deal between the two series. There were somewhat lower concentrations of moisture and ash and correspondingly higher calorific values on the second occasion. There were also significantly lower fluorine concentrations on the second occasion, which was responsible for the lower HF concentrations observed in the flue gas, as described in Section 5.4.2.

Calculations were performed to predict gas volumes and fly ash concentrations resulting from the combustion of coal. Results for the gas volume expected from 1 kg of coal are presented in Table 4. The predicted concentrations of CO_2, SO_2, HCl, and HF are also given in this table. All of the predictions about the flow rate and composition of the flue gas are based on the assumption that the excess air produces a final O_2 concentration of 4% by volume. The information in Table 4 was used in mass balance calculations that are reported in Section 6.

Samples of the coal were ashed at Southern Research at 750 °C and analyzed for the major metals and non-metals. Analysis for the metals was performed by AAS; analysis for the non-metals was based on colorimetry and ion chromatography. The analytical data are summarized in Table 5. The data given in this table are averages and standard deviations for each set of samples.

Data on trace elements in the coal are presented in Tables 6, 7, and 8. The first of these three tables gives averages and standard deviations for each metal in each test series. The latter two tables give data for daily samples in each series. The data on trace metals concentrations were obtained by essentially two methods or combinations of methods:

1) ICP and AAS methods were employed in the Analytical and Physical Chemistry Department of Southern Research. Arsenic, antimony, cadmium, lead, and selenium were determined by hydride generation or graphite furnace AAS procedure; mercury was determined by cold vapor AAS.

2) NAA was performed at the Research Reactor Facility at the University of Missouri-Columbia. Four of the metals of interest could not be determined at Missouri's reactor facility (beryllium, cadmium, copper, and lead). The data obtained by NAA were therefore augmented by determinations of these four metals by AAS (flame injection) in the chemical laboratory of the Environmental Sciences Department of Southern Research. Also, phosphorus was determined colorimetrically to augment the NAA data.

The coal was digested in preparation for ICP analysis; it was analyzed directly, without any preparation, when NAA was used. The supplementary determinations of the four metals and phosphorus by AAS, on the other hand, were performed after the coal had been ashed, with the assumption that none of these four elements would be lost in the ashing of the coal.

A recurring feature of the comparative analysis of the coal for trace elements is that ICP yielded lower concentrations for most of the elements than NAA did. At the end of the program, we learned that there is a difficulty of completely digesting coal ash or fly ash with the EPA-recommended method. Incomplete sample dissolution is certainly a probable cause for the lower element concentrations found by ICP. In addition, comparison of analyses of coal and fly ash from the National Institute of Science and Technology (Standard Reference Materials) showed that ICP yielded low concentrations of the trace elements, whereas NAA was accurate in nearly every instance (see Appendix D). Accordingly, the data in Tables 6, 7, and 8 based on NAA must be regarded as more dependable than the data based on ICP.

Pyrite rejected from the coal after crushing proved to be a highly variable substance. On two occasions during the baseline test series there was no pyrite to be removed from the collection chambers. For the samples that were obtained, the analytical data for the major components are given in Table 9. The line of data across the bottom gives loss-on-ignition figures that show the variability of the sample composition. Losses on ignition ranged from 34.2 to 91.9%, which indicated that the material was sometimes largely inorganic (pyritic) and sometimes highly combustible (that is, high in coal content). The percentage of the residue from ignition that is reported as Fe_2O_3 varied inversely with the loss on ignition. The concentration of sulfur varied widely on a relative basis, although not on an absolute basis. Most of the sulfur passed off in the off-gases during ignition, presumably as SO_2 mainly; only a small fraction of the sulfur was retained in the residue as sulfate (SO_3). (Note: the weight ratio of sulfur to iron in the compound pyrite, FeS_2, is 1.15.)

Pyrite analyzed by ICP/AAS methods for trace elements yielded the data in Table 10. The compositions of the pyrite samples were again shown to be highly variable.

Samples of the pulverized coal were treated in the same manner as ash to determine whether either Cr(VI) or As(III) could be detected. Neither of these species was observed. For Cr(VI), all that can be said is that the concentration extracted into alkaline solution corresponded to a concentration in the coal of <4 μg/g (compared to a total chromium concentration of just about twice that limit, 8-9 μg/g). For As(III), the concentration extracted corresponded to a concentration in the coal of <0.1 μg/g, not more than 4% of the total concentration of arsenic.

Table 3
Proximate and Ultimate Analyses of the Coal

	Baseline, September 1991				Low NO$_x$, January 1992			
Coal property	9/18	9/19	9/20	9/21	1/14	1/15	1/16	1/17
Proximate:								
% Moisture	10.63	10.03	9.60	9.07	9.35	9.67	9.40	8.55
% Ash	8.99	8.99	9.10	9.13	8.28	8.05	8.28	8.56
% Volatile	34.91	34.99	35.07	35.34	36.08	36.30	36.47	36.96
% Fixed	45.47	45.99	46.23	46.46	46.29	45.98	45.85	45.93
Btu/lb	11770	11877	11921	11960	12051	12048	12047	12100
Ultimate:								
% Carbon	65.48	65.70	65.77	66.64	66.80	67.24	67.01	67.42
% Hydrogen	4.40	4.37	4.31	4.50	4.60	4.42	4.57	4.55
% Nitrogen	1.43	1.39	1.33	1.31	1.45	1.47	1.46	1.46
% Sulfur	2.90	3.00	2.95	2.75	2.78	2.88	2.86	2.88
% Oxygen	5.77	6.52	6.94	6.60	6.74	6.27	6.42	6.58
% Chlorine	0.19	0.17	0.19	0.19	0.16	0.16	0.18	0.18
ppm Fluorine	76	76	66	100	59	55	59	63

Table 4
Production of Gases and Fly Ash
from the Coal[a]

	Baseline, September 1991				Low NO$_x$, January 1992			
	9/18	9/19	9/20	9/21	1/14	1/15	1/16	1/17
Gas volume,[b] Nm^3	8.976	8.998	8.898	9.056	9.102	9.124	9.133	9.171
Fly ash, g/Nm^3	10.02	10.08	10.23	10.08	9.10	8.82	9.06	9.33
CO$_2$, % vol.	14.7	14.7	14.8	14.7	14.7	14.8	14.7	14.7
SO$_2$, ppmv	2420	2520	2490	2280	2290	2370	2350	2360
HCl, ppmv	143	129	145	142	119	119	133	133
HF, ppmv	10.2	10.3	8.9	10.4	7.8	7.3	7.8	8.7

[a] At 4% O$_2$ on the dry basis.
[b] From 1 kg of coal.

Table 5
Average Mineral Concentrations in Coal Ash
(concentrations in weight percentages)

	Baseline Sept. 1991	Low NO_x Jan. 1992
Li_2O	0.02 ± 0	0.02 ± 0
Na_2O	0.81 ± 0.19	0.65 ± 0.04
K_2O	2.4 ± 0.1	2.4 ± 0.1
MgO	0.88 ± 0.01	0.86 ± 0.02
CaO	4.5 ± 0.4	4.9 ± 0.3
Fe_2O_3	18.2 ± 1.4	18.8 ± 0.2
Al_2O_3	18.6 ± 0.4	19.0 ± 0.3
SiO_2	47.4 ± 1.7	47.5 ± 0.5
TiO_2	1.1 ± 0	1.1 ± 0.1
P_2O_5	0.23 ± 0.02	0.20 ± 0.01
SO_3	4.0 ± 0.5	3.2 ± 0.6
LOI[a]	90.8 ± 0.1	91.8 ± 0.5

[a] Refers to loss on ignition from the coal; ash was analyzed after ignition.

Table 6
Comparison of Trace Element Concentrations in Coal
for Different Test Series by Different Methods
(concentrations in μg/g)

	Baseline, September 1991		Low-NO$_x$, January 1992	
	ICP/AAS	NAA/AAS[a]	ICP/AAS	NAA/AAS[a]
As	1.9 ± 0.4	4.2 ± 0.6	<2.3	3.6 ± 0.3
Ba	27.0 ± 4.7	54 ± 8	35.8 ± 3.4	57 ± 5
Be	0.66 ± 0.15	<10	1.3 ± 0.8	<10
Cd	1.6 ± 0.4	<2	2.8 ± 0.1	2 ± 0
Co	1.6 ± 0.7	3.0 ± 0.3	<0.5	2.5 ± 0.1
Cr	5.5 ± 1.4	17 ± 3	9.0 ± 0.6	17 ± 1
Cu	5.7 ± 0.4	14 ± 9	15.5 ± 2.1	13 ± 3
Hg	0.064 ± 0.005	<0.05	0.077 ± 0.045	<0.04
Mn	16.8 ± 2.5	33 ± 21	16.4 ± 1.1	16.0 ± 4.1
Mo	4.5 ± 0.8	8.6 ± 1.7	9.0 ± 1.4	10.6 ± 0.3
Ni	6.7 ± 1.1	<13	6.8 ± 0.9	<16
P	13.1 ± 4.2	92	23.9 ± 3.4	73
Pb	<6	18 ± 1	17.0 ± 1.1	20 ± 3
Sb	<2	1.2 ± 0.2	<4	1.5 ± 0.1
Se	0.58 ± 0.02	2.3 ± 0.3	2.1 ± 0.4	1.6 ± 0.7
V	46.7 ± 14.8	53 ± 32	69.2 ± 6.4	78 ± 4

[a] Be, Cd, Cu, and Pb by flame-injection AAS; P by colorimetric procedure.
All determined on coal-ash.

Table 7
Comparison of Trace Metal Concentrations in Daily Baseline Coal Samples Analyzed by Different Methods
(data in $\mu g/g$)

	9/18/91		9/19/91		9/20/91		9/21/91	
	ICP/AAS	NAA/AAS[a]	ICP/AAS	NAA/AAS[a]	ICP/AAS	NAA/AAS[a]	ICP/AAS	NAA/AAS[a]
As	1.65	4.0	2.04	5.1	1.55	4.0	2.34	3.7
Ba	28.2	62	24.0	44	22.7	58	33.2	52
Be	<0.5	<10	0.60	<10	0.56	<10	0.83	<10
Cd	2.15	<2	1.75	<2	1.57	2	1.12	2
Co	0.99	2.7	2.10	3.4	2.23	3.1	1.05	2.7
Cr	4.04	15	5.2	18	7.41	21	5.24	15
Cu	5.36	20	6.26	22	5.93	6	5.43	6
Hg	0.061	<0.041	0.069	<0.039	0.068	<0.053	0.059	<0.045
Mn	19.6	24	18.2	64	14.5	25	14.8	18
Mo	4.76	7.6	5.14	9.2	4.56	10.8	3.36	7.0
Ni	6.61	<11	7.50	<11	7.60	13	5.15	<11
P	19.2	91.7	12.4	91.7	10.7	78.0	9.94	81.9
Pb	<5	16	8.2	18	<5	18	<5	18
Sb	<2	1.0	<2	1.2	<2	1.4	<2	1.2
Se	0.54	2.1	0.60	2.0	0.57	2.7	0.56	2.4
V	33.9	42	48.2	29	37.7	101	67.0	40

[a] Be, Cd, Cu, and Pb via AAS (flame aspiration). Each for coal ash.

Table 8
Comparison of Trace Element Concentrations in Daily Low-NO$_x$ Coal Samples Analyzed by Different Methods
(data in μg/g)

	1/14/92		1/15/92		1/16/92		1/17/92	
	ICP/AAS	NAA/AAS[a]	ICP/AAS	NAA/AAS[a]	ICP/AAS	NAA/AAS[a]	ICP/AAS	NAA/AAS[a]
As	2.53	3.4	<2	3.4	<2	4.0	2.85	3.8
Ba	39.4	62	37.9	59	32.5	54	33.2	52
Be	0.66	<10	0.57	<10	1.96	<10	2.05	<10
Cd	1.99	2	2.17	2	2.12	2	2.04	2
Co	<0.5	2.6	<0.5	2.4	<0.5	2.4	<0.5	2.5
Cr	9.04	16	8.15	17	9.51	17	9.40	18
Cu	18.5	12	13.8	17	14.6	10	15.0	12
Hg	0.136	<0.032	0.068	<0.031	0.027	<0.038	0.076	<0.029
Mn	17.5	19.7	15.2	18.2	15.8	18.4	17.1	20.8
Mo	10.2	10.9	7.01	10.8	8.90	10.2	9.89	10.5
Ni	7.12	<15	5.43	<16	7.18	<15	7.37	<16
P	28.8	67.6	21.4	68.9	21.6	67.5	23.7	66.3
Pb	18.4	18	16.9	18	17.0	18	15.6	24
Sb	<4	1.5	<4	1.5	<4	1.6	<4	1.4
Se	1.53	1.77	2.07	0.66	2.42	2.28	2.20	1.67
V	63.8	79	67.5	73	66.8	75	78.5	83

[a] Be, Cd, Cu, and Pb via AAS (flame aspiration). Each for coal ash.

Table 9
Mineral Concentrations in Daily Pyrite Samples from Baseline and Low-NO_x Test Series
(concentrations in weight percentage)

	September 1991		January 1992			
	9/18	9/19	1/14	1/15	1/16	1/17
Li_2O	0.01	0.01	0.02	0.02	0.01	0.02
Na_2O	0.10	0.71	0.57	0.72	1.1	0.57
K_2O	0.5	3.4	2.5	2.7	4.5	3.4
MgO	0.19	1.43	0.86	0.93	2.5	1.3
CaO	0.1	1.1	5.7	0.91	3.1	1.6
Fe_2O_3	81.6	20.3	7.1	27.1	7.5	12.1
Al_2O_3	5.3	18.4	20.3	17.6	20.2	21.6
SiO_2	10.2	52.0	55.6	46.9	55.8	55.6
TiO_2	0.2	0.9	1.2	0.9	0.9	1.2
P_2O_5	0.23	0.54	0.13	0.16	0.18	0.15
SO_3	0.19	0.56	2.5	0.49	1.5	0.67
LOI[a]	34.2	64.7	89.2	84.6	64.4	91.9

[a] Determined for pyrite as received. Minerals determined after ashing.

Table 10
Trace Element Concentrations in Daily Pyrite Samples[a]
(data in $\mu g/g$)

	Baseline, September 1991		Low NO$_x$, January 1992			
	9/18/91	9/19/91	1/14/92	1/15/92	1/16/92	1/17/92
As	170	31.1	<2.0	6.0	<2.0	<2.0
Ba	40.5	160	42.9	64.4	202	38.1
Be	<10	<10	12.8	<0.5	6.7	1.7
Cd	44.3	<10	0.49	5.1	32.6	0.89
Co	84.6	13.7	<0.5	<0.5	3.4	<0.5
Cr	<10	62.7	37.7	10.2	200	5.7
Cu	23.8	31.1	12.6	26.9	67.3	10.6
Hg	1.34	0.076	0.080	<0.060	0.062	<0.060
Mn	32.2	116	28.0	18.9	91.5	13.3
Mo	9.3	13.9	12.4	6.3	357	4.3
Ni	405	63.7	9.8	8.0	129	8.4
P	271	261	14.4	52.8	79.5	13.8
Pb	493	107	3.7	24.4	13.7	6.2
Sb	2.28	<2	<4.0	<4.0	4.8	<4.0
Se	<1.0	1.4	2.1	1.5	5.3	1.1
V	136	66.5	1097	46.8	641	12.6

[a] Concentrations derived by ICP/AAS methods.

5.2 WATER

Water used for wetting the bottom ash and transporting it to the ash pond (referred as "boiler seal" water) was analyzed for trace metals and for semi-volatile organics. Table 11 gives the concentrations for the trace elements in water samples from both test series. The analysis of the organics examined the water samples for the presence of approximately 80 compounds on the list of target compounds subsequently described in Section 5.4.5. None of the compounds was detected. For all of the compounds but one, the maximum concentration that could have been present was 15 ng/mL; for the exception, benzidine, the limit was 60 ng/mL.

Table 11
Concentrations of Elements in Boiler Seal Water
(concentrations in μg/mL)

	Baseline testing	Low-NO$_x$ testing
As	0.0251 ± 0.0370	Neg[a]
Ba	0.0111 ± 0.0044	0.0145 ± 0.0040
Be	0.0056 ± 0.0004	0.0009 ± 0.0002
Cd	0.0017 ± 0.0007	Neg[a]
Co	0.0158 ± 0.0034	0.0050 ± 0.0014
Cr	0.0023 ± 0.0045	0.0044 ± 0.0103
Cu	0.0314 ± 0.0202	0.0028 ± 0.0016
Hg	<0.0003	<0.0003
Mn	0.0106 ± 0.0095	0.0095 ± 0.0102
Mo	Neg[a]	Neg[a]
Ni	0.0322 ± 0.0054	0.0128 ± 0.0021
P	0.0351 ± 0.0152	0.0145 ± 0.0041
Pb	0.0362 ± 0.0209	0.0145 ± 0.0041
Sb	Neg[a]	0.0154 ± 0.0041
Se	<0.012	0.0034 ± 0.0028
V	0.0108 ± 0.0033	0.0279 ± 0.0156

[a] The ICP signal was, on the average, negative, implying interference not compensated for. Presumably, the true concentration was very close to zero.

5.3 BOTTOM ASH AND FLY ASH FROM THE ECONOMIZER AND ESP HOPPERS

Although metal contents were the focus of interest in the ash compositions, the non-metallic element carbon was also of interest because of its possible elevation as the result of low-NO_x combustion. Table 12 presents the results of determinations of carbon and incidental determinations of hydrogen and nitrogen in samples of ESP hopper ash. These data indicate that during the time of the sampling of air toxics at the test site, the low-NO_x combustion conditions increased carbon in the ESP ash by about one-half. The ESP hopper ash referred to here and in other places later in this section was a composite of ash from the hot-side ESP, there being no sample recovered from the cold-side ESP. The prevailing conclusion from long-term operations, however, is contrary to the implications of Table 12 as to the effect of low-NO_x combustion on carbon content of the ash. That conclusion, as stated previously in this report, is that low-NO_x combustion at Site 110 does not produced enhanced carbon emission with the ash.

The oxides of eleven elements that constitute close to 100% of most ashes from the combustion of coal are compared for coal ash, bottom ash, economizer ash, and ESP hopper ash in Table 13. There are no evident lessons to be learned about the partitioning of the major metals and non-metals between the different forms of ash. That is, each of the major elements occurs in fly ash at either location (economizer or ESP) or occurs in bottom ash at roughly the same relative concentration at which it appears in the original coal. As for most of the metals (magnesium, calcium, iron, aluminum, and titanium), the absence of significant partitioning is not surprising, for none of these is notably volatile. The alkali metals, on the other hand, may be vapors in the furnace; this is true for sodium and potassium, if not for lithium. Nevertheless, no partitioning of the alkali metals is evident.

Distributions of the trace metals in bottom ash, economizer ash, and ESP hopper ash are revealed in Tables 14 and 15 for the baseline and low-NO_x test series, respectively. There are some expected trends and some unexpected trends in these data, as indicated below:

- In the baseline samples, arsenic occurred at a much lower concentration in the bottom ash than in the fly ash from either location. This was expected because of the volatility of this element. The appearance of arsenic at higher concentrations at the economizer than at the ESP, on the other hand, is anomalous.

- Mercury was not detected in any of the ashes. The absence of mercury at any location is consistent with this element's having the highest volatility of any of those considered.

- Antimony was not detected in the bottom ash but was found in fly ash from either location. The similarity of the distributions of arsenic and antimony corresponds to what is known about their volatilities – higher than the volatilities of most of the metals but lower than those of mercury and selenium.

- Selenium, like mercury, was not found in any of the ashes from the baseline test series and was found at very low concentrations in the ashes from the low-NO_x series (these low concentrations were consistent with the upper limits reported for the first data set). Selenium was expected to rank second highest, next to mercury, in volatility.

A broader perspective is given in Tables 16 and 17 for the two test series. These tables give average elemental concentrations in coal ash, bottom ash, economizer ash, ESP hopper ash, and filter ash from the Multiple Metals Train at the ESP inlet. In these tables, for convenience, only averages from the four daily samples are presented. The elemental concentrations in coal ash, it must be said, are hypothetical values, calculated by dividing elemental concentrations in the coal by ash concentrations in the coal. Some of the conclusions that can be drawn from these tables are as follows:

- Differences between element concentrations in the bottom ash or fly ash (in any of the four locations) and the corresponding concentrations in the coal ash should occur when there is significant volatility. Such differences are most notable for mercury and selenium, the most volatile elements; these elements are less concentrated in the bottom ash or fly ash than in the coal ash.

- Differences in some of the elements between bottom ash or fly ash and coal ash are indicative of experimental error. For example, cobalt is reported as below the detection limit (<0.5 μg/g) in the coal ash in Table 17 but as concentrations around 20-25 μg/g in the bottom ash and fly ash. This contrast is obviously absurd; it must be due to an error in the determination of cobalt in the coal.

- Differences between element concentrations in the ESP ash and the metals train ash are plausible in some instances and not plausible in others. The difference in the temperature in the ESP (700 °F) and the sampling train (250 °F at the filter) can make the concentration of a volatile element higher in the sample from the train. The differences for selenium are likely to be the result of this temperature difference. The difference for barium in Table 17, on the other hand, cannot be interpreted as an effect of the volatility of barium but must be attributed to analytical error.

All of the data on metals discussed above were determined by ICP and AAS methods in combination. Data in Tables 18 and 19 compare the concentrations of the metals in ESP ashes that were analyzed by both ICP/AAS and NAA. The data are in reasonable agreement except for antimony and selenium in Table 18 and for arsenic, antimony, and molybdenum in Table 19.

Samples of economizer and ESP hopper ash were analyzed for semi-volatile organic compounds. Except for certain phthalate esters, none of the 80 or so compounds on the list of target compounds discussed in Section 5.4.5 was found. Nearly every sample contained one or more phthalate esters at the time of analysis; these compounds are believed to have been present as the result of contamination of samples in the laboratory. For all but one of the compounds not detected, the maximum concentration that could have been present was 0.75 μg/g; for the exception, benzidine, the limit was 3.0 μg/g.

Analyses of the ash samples included determinations of Cr(VI) and As(III)/As(V). The data for Cr(VI) are given in Table 20. Cr(VI) was not found in pyrite or bottom ash. It was found in economizer ash and ESP hopper ash, however, at levels around 5% of the total chromium. Neither form of arsenic was found in extracts of pyrite or bottom ash (the concentration limit for the original solid was 0.1 μg/g). No As(III) was found in extracts of economizer ash or ESP hopper ash either, but As(V) was observed in these extracts. The concentration of As(V) extracted was highly variable but accounted for only a small percentage of the total arsenic in any instance. (Analysis of the SRM ash from the National Institute of Science and Technology, No. 1633a, on the other hand, recovered about 15% of the total arsenic as As(III) and about 30% as As(V) in aqueous extracts).

Table 12
Carbon, Hydrogen, and Nitrogen in ESP Hopper Ash

	Baseline September 1991	Low NO_x January 1992
Carbon	5.4 ± 0.5	7.3 ± 1.1
Hydrogen	0.0 ± 0	0.0 ± 0
Nitrogen	0.05 ± 0.01	0.05 ± 0.01

Table 13
Average Mineral Concentrations in Ashes from Various Sources
(concentrations in weight percentages)

Baseline, September 1991

	Coal ash	Bottom ash	Econ. ash	ESP ash
Li_2O	0.02 ± 0	0.02 ± 0	0.02 ± 0.01	0.02 ± 0
Na_2O	0.81 ± 0.19	0.59 ± 0.13	0.71 ± 0.34	0.56 ± 0.02
K_2O	2.4 ± 0.1	1.9 ± 0.2	1.6 ± 0.1	2.5 ± 0.1
MgO	0.88 ± 0.01	0.91 ± 0.02	0.87 ± 0.02	0.91 ± 0.01
CaO	4.5 ± 0.4	5.5 ± 0.4	9.7 ± 1.4	5.5 ± 0.2
Fe_2O_3	18.2 ± 1.4	20.9 ± 1.4	21.7 ± 1.0	18.2 ± 0.4
Al_2O_3	18.6 ± 0.4	18.4 ± 0.5	16.6 ± 0.8	19.5 ± 0.4
SiO_2	47.4 ± 1.7	50.8 ± 1.5	44.1 ± 1.9	50.2 ± 0.2
TiO_2	1.1 ± 0	1.0 ± 0.1	1.0 ± 0.1	1.2 ± 0
P_2O_5	0.23 ± 0.02	0.21 ± 0.01	0.37 ± 0.04	0.22 ± 0.01
SO_3	4.0 ± 0.5	0.22 ± 0.07	2.2 ± 1.1	0.89 ± 0.06
LOI	90.8 ± 0.1	0.9 ± 0.5	3.4 ± 3.2	4.3 ± 2.3

Low NO_x, January 1992

	Coal ash	Bottom ash	Econ. ash	ESP ash
Li_2O	0.02 ± 0	0.02 ± 0	0.02 ± 0	0.02 ± 0
Na_2O	0.65 ± 0.04	0.62 ± 0.04	0.62 ± 0.02	0.74 ± 0.03
K_2O	2.4 ± 0.1	2.2 ± 0.1	2.0 ± 0	2.6 ± 0.1
MgO	0.86 ± 0.02	0.93 ± 0.02	0.90 ± 0.01	1.1 ± 0.3
CaO	4.9 ± 0.3	5.8 ± 0.3	11.4 ± 0.2	5.3 ± 0.4
Fe_2O_3	18.8 ± 0.2	22.7 ± 0.3	20.0 ± 2.6	18.5 ± 0.9
Al_2O_3	19.0 ± 0.3	18.7 ± 0.2	17.1 ± 0.4	19.9 ± 0.3
SiO_2	47.5 ± 0.5	48.4 ± 0.6	41.4 ± 0.6	49.0 ± 0.6
TiO_2	1.1 ± 0.1	0.9 ± 0	1.1 ± 0	1.1 ± 0
P_2O_5	0.20 ± 0.01	0.20 ± 0.01	0.44 ± 0.02	0.20 ± 0.01
SO_3	3.2 ± 0.6	0.11 ± 0.02	2.9 ± 0.6	0.65 ± 0.06
LOI	91.8 ± 0.5[a]	1.4 ± 0.5	0.4 ± 0.3	7.8 ± 1.1

[a] Refers to loss on ignition of coal; ash was analyzed after ignition.

Table 14
Comparison of Trace Elements in Bottom, Economizer, and ESP Ashes from Baseline Samples
(September 1991)
(all data by ICP/AAS, $\mu g/g$)

	9/18/91			9/19/91			9/20/91			9/21/91		
	Bott	Econ	ESP	Bott	Econ	ESP	Bott	Econ	ESP	Bott	Econ	ESP
As	3.54	71.5	35.6	2.43	193	35.1	3.83	140	31.8	2.32	79.7	39.3
Ba	433	510	595	551	551	375	470	383	490	617	398	475
Be	8.3	10.3	14.1	11.1	11.1	<10.0	9.4	14.3	11.7	11.1	9.9	13.0
Cd	10.5	17.0	22.2	14.2	14.3	19.7	11.5	29.4	11.3	16.6	25.5	20.5
Co	20.1	24.6	36.1	33.0	33.0	25.7	32.6	38.3	35.2	30.5	27.1	40.6
Cr	127	236	223	161	369	161	141	307	172	165	229	179
Cu	91.3	59.2	61.1	67.7	67.7	67.6	59.0	71.5	69.8	99.6	54.7	76.2
Hg	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Mn	217	334	242	254	254	201	251	302	251	279	286	213
Mo	17.1	94.4	129	24.0	99.8	69.1	23.4	99.9	82.3	27.1	67.0	104
Ni	84	109	103	135	135	95	108	137	114	134	110	146
P	145	446	252	193	193	91	159	282	189	240	322	218
Pb	102	70.2	167	118	98.8	150	122	91.4	167	109	70.0	176
Sb	<2	7.7	3.5	<2	30.2	20.7	<2	13.9	<2	<2	7.8	<2
Se	<1	2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
V	614	750	697	649	649	510	599	774	579	802	686	602

Table 15
Comparison of Trace Elements in Bottom, Economizer, and ESP Ash from Low-NO_x Samples
(January 1992)
(all data by ICP/AAS, μg/g)

	1/14/92		1/15/92		1/16/92			1/17/92		
	Bott	ESP	Bott	ESP	Bott	Econ	ESP	Bott	Econ	ESP
As	--[a]	16.4	--[a]	21.1	--[a]	--[a]	18.3	--[a]	--[a]	27.8
Ba	595	458	572	366	530	558	541	516	558	504
Be	4.67	4.57	6.16	4.68	7.85	8.93	1.43	5.94	9.14	1.08
Cd	24.7	24.1	26.9	23.4	26.5	40.1	26.8	26.5	40.2	26.6
Co	23.6	21.6	22.3	18.0	22.3	22.7	25.2	21.1	25.0	23.9
Cr	156	160	171	134	191	365	190	172	394	171
Cu	44.5	62.9	46.1	60.8	44.2	89.1	69.2	43.9	115	63.3
Hg	<0.06	<0.06	<0.06	<0.06	<0.06	<0.15	<0.06	<0.06	<0.15	<0.06
Mn	231	190	218	171	228	318	218	211	301	200
Mo	37.3	92.4	39.6	85.1	47.1	161	116	43.2	183	115
Ni	103	93.3	107	76.8	114	148	117	111	135	106
P	201	174	208	158	194	485	188	198	514	179
Pb	8.17	113	9.10	89.5	6.83	40.0	142	7.64	50.6	138
Sb	<4	9.21	<4	9.33	<4	32.7	9.77	<4	34.3	14.2
Se	0.24	0.57	0.28	0.52	0.26	0.40	0.45	<0.20	0.40	0.59
V	754	657	894	703	970	1231	926	941	1301	764

[a] The data obtained for As are believed to be erroneous because they are based on ICP data in which aluminum interfered. The determination of arsenic by HGAAS yielded the corresponding data for As in Table 14. The use of HGAAS is preferred over the determination by ICP but was not used here.

Table 16
Further Comparison of Trace Element Concentrations in Ash from the Boiler to the Hot-side ESP — Baseline Testing, September 1991
(all data from ICP/AAS, µg/g)

	Coal ash[a]		Bottom		Economizer		ESP		Metals train, inlet	
	Avg.	RSD%	Avg.	RSD%	Avg.	RSD%	Avg.	RSD%	Avg.	RSD%
As	21.1	19	3.0	25	103	80	35.4	9	26.6	14
Ba	298	17	518	16	460	18	484	19	284	33
Be	6.9	22	10.0	14	11.4	18	12.2	14	8.4	26
Cd	18.2	27	13.2	21	21.6	33	18.4	26	89.4	95
Co	17.6	42	29.0	21	30.8	20	34.4	18	23.7	16
Cr	60.4	25	148	12	285	23	184	15	140	6
Cu	63.5	8	79.1	25	63.3	12	68.7	9	63.4	19
Hg	0.71	8	<0.05	--	<0.05	--	<0.05	--	0.32	59
Mn	185	16	250	10	294	11	227	10	160	39
Mo	49.3	18	22.9	18	90.3	17	86.8	33	90.0	18
Ni	75.2	15	115	21	123	12	114	20	96.6	9
P	144	33	184	23	311	34	187	37	166	18
Pb	<90	--	113	8	82.6	18	165	7	165	13
Sb	<20	--	<2	--	14.9	71	7.0	13	17.6	20
Se	6.3	5	<1	--	<1	--	<1	--	3.54	36
V	515	31	666	14	715	8	597	13	540	15

[a] Calculated as µg element/g coal ÷ % ash/100.

Table 17
Further Comparison of Trace Element Concentrations in Ash from the Boiler to the Hot-side ESP — Low-NO$_x$ Testing, January 1992
(all data from ICP/AAS, μg/g)

	Coal ash[a]		Bottom		Economizer		ESP		Metals train, inlet	
	Avg.	RSD%	Avg.	RSD%	Avg.	RSD%	Avg.	RSD%	Avg.	RSD%
As	<28.2	-	–	19	–	7	–	10	11.8	32
Ba	432	11	553	7	558	0	467	16	938	9
Be	18.2	53	6.15	21	9.04	2	2.94	66	8.2	21
Cd	25.1	6	26.1	4	40.2	0.2	25.2	7	11.9	58
Co	<0.5	-	22.3	5	23.8	7	22.2	14	24.5	10
Cr	109	5	170	9	380	5	164	14	126	27
Cu	186	13	44.7	2	102	18	64.0	6	61.8	27
Hg	0.92	58	<0.06		<0.15	-	<0.06	-	0.19	38
Mn	198	5	222	4	310	4	195	10	176	11
Mo	108	16	41.8	10	172	9	102	15	121	22
Ni	81.6	12	109	4	142	6	98.3	18	97	6
P	81.5	4	200	3	500	4	175	7	149	63
Pb	205	8	7.94	12	45.3	17	121	20	90.9	24
Sb	<4	-	<4		33.5	3	10.6	23	42.5	125
Se	24.8	18	0.24	3	0.40	0	0.53	12	16.4	2
V	834	7	890	11	1266	4	762	15	632	12

[a] Calculated as μg element/g coal ÷ % ash/100.

Table 18
Comparison of Trace Element Concentrations in Baseline ESP Samples by ICP and NAA Methods
(data in μg/g)

	ICP/AAS[a]	NAA[a]
As	35 ± 3	39 ± 3
Ba	484 ± 90	464 ± 89
Co	34 ± 6	31 ± 1
Cr	184 ± 27	175 ± 6
Hg	<0.05	<0.03
Mn	227 ± 24	239 ± 1
Mo	120 ± 70	82 ± 5
Ni	115 ± 22	87 ± 6
Sb	–[b]	13 ± 1
Se	<1	2.1 ± 0
V	597 ± 77	585 ± 61

[a] The uncertainty figure is the standard deviation.
[b] Wide variation: results of <2, <2, 3.5, and 20.7.

Table 19
Comparison of Trace Element Concentrations in Low-NO$_x$ ESP Samples by ICP and NAA Methods
(data in μg/g)

	ICP/AAS[a]	NAA[a]
As	15.8 ± 2.9	37 ± 4
Ba	553 ± 37	474 ± 40
Co	22 ± 1	26 ± 1
Cr	172 ± 14	178 ± 12
Hg	<0.06	<0.04
Mn	222 ± 9	200 ± 4
Mo	42 ± 4	97 ± 12
Ni	109 ± 5	76 ± 18
Sb	<4	17 ± 2
Se	0.24 [illegible]	1.5 ± 0.4
V	89[illegible]	733 ± 75

[a]The uncertainty figure is the standard deviation.

Table 20
Data on Chromium Speciation in Solids

Type of testing	Type of sample	Date of sample	Total Cr, $\mu g/g$	Cr (VI)	
				$\mu g/g$	% of total
Baseline	Pyrite	9/19	62.7	<4	6
	Bottom ash	all	148 (avg)	<4	<3
	Economizer ash	9/18	236	7.0	3.6
		9/19	369	18.2	4.9
		9/20	307	15.2	5.0
		9/21	229	8.8	3.9
	ESP hopper ash	9/18	223	16.8	7.5
		9/19	161	10.7	6.6
		9/20	172	9.6	5.6
		9/21	179	10.5	5.9
Low-NO_x	Pyrite	all	5.7-200	<4	-[a]
	Bottom ash	all	172	<4	<3
	Economizer ash	1/16	365	17.7	4.8
		1/17	394	23.6	6.0
	ESP hopper ash	1/14	160	<4	<3
		1/15	134	4.0	3.0
		1/16	190	5.2	2.7
		1/17	171	6.9	4.0

[a] Cannot be evaluated because of the variability of pyrite compositions.

5.4 COMPONENTS OF THE FLUE GAS STREAMS

5.4.1 Trace Elements

Total concentrations of the elements. Tables 21 and 22 present summaries of the data on the concentrations of trace elements found in the flue gas streams at the hot-side ESP inlet and the cold-side ESP outlet. The first of these tables gives the data for samples collected during the baseline test series; the second table gives the data for the low-NO_x series. In each table, there are data for four test dates; the first of these dates in either table is the occasion when the cold-side ESP was energized, whereas the remaining three dates were times when the cold-side ESP did not operate.

For each date, there are six concentration terms for each element. Three values are for samples from the inlet: 1) the front half of the sampling train (particulate matter), 2) the back half (nominally materials in the vapor state but actually not just vaporous material, as will be explained), and 3) finally the sum of the values from the front and back halves. The three remaining concentration terms are the corresponding values from the outlet sampling location.

Some of the results for the back half of the sampling train can hardly be just for vaporous substances collected in the impingers. Reasons for this observation are cited in the following discussion:

- There must be anomalous results in the table that are due to errors in sampling or analysis. One example is the value 768 $\mu g/Nm^3$ of cadmium reported for the ESP inlet for September 18. Another is the 223 $\mu g/Nm^3$ of chromium reported for the ESP inlet on January 14. Other data that must be erroneous are several high concentrations of manganese in the back halves of the outlet samples. These high concentrations of manganese are attributed to some form of carry-over of permanganate solution from the final impingers ($H_2SO_4/KMnO_4$ for mercury collection) to the first impingers (HNO_3/H_2O_2 for collecting mercury and all other metals).

- Even some relatively small concentrations for the back half that are less obvious than those cited above can hardly represent actual amounts of vapor that penetrated the filter at 250 °F. For example, the values for chromium in Table 21 for the back half of the sampling train, ranging from 1.4 to 11.7 $\mu g/m^3$, are doubtful for the vapor of this element. Presumably, if these values are not due to an analytical error of some type, they represent slippage of fine particulate matter past the filter.

Despite the comments above, the amounts of certain other elements partitioned between the front and back halves of the sampling train probably give true indications of occurrences in the particulate and vapor states. The inlet data for arsenic in Table 21, for example, indicate that less than 1% of this element occurred as the vapor at the filter temperature of 250 °F. This observation for arsenic, sometimes regarded as one of the more volatile trace metals, does not, of course, address the question of the state of arsenic in the hot-side ESP at 700 °F and does not reveal the fate of the element in the precipitation process.

The data for selenium suggest substantial fractions of this element occurred in the vapor state in the sampling train. This is a valid conclusion, although there are some troublesome aspects to the data on selenium, such as outlet concentrations that exceeded inlet concentrations in Table 21. The data for selenium in ashes from locations other than the sampling trains, it will be recalled, showed very low concentrations of selenium. Consequently, much of the selenium found in the front half of the sampling train (far from the total collected) must have been found there because deposition occurred as the result of the filter having a lower temperature than the duct sampled.

The data for mercury show some surprising features. For example, there are concentrations for the particulate catch that are higher than the concentrations for the impinger catch. This was not expected, because of the anticipation that mercury would be mainly in the vapor state. In addition, there are results that show higher total concentrations of mercury at the inlet than at the outlet; little collection of mercury in the ESP from the predominant vapor state was expected. Some of the anomalies of the data for mercury were almost certainly caused by incomplete data for mercury in the impingers of the sampling train. Generally, little or no mercury was found in the peroxide impingers. Belatedly, the procedure for analyzing the peroxide impingers for mercury was tested and found inadequate, because mercury spikes could not be recovered from the peroxide medium. The origin of the problem lies in the need to destroy excess peroxide before the determination of mercury is started. Thus, the data for mercury in Tables 21 and 22 should be disregarded, and the data obtained from samples from another source, presented later in Tables 25 and 26, should be accepted instead.

Examination of the data for antimony suggests that there is little evidence for occurrence of this element in the vapor state within the sampling train. The conclusion for this element based on the data in Tables 21 and 22 is in accord with the conclusion reached earlier from the data on ashes from various locations.

The data for the front halves of the outlet samples from the low-NO_x sampling (Table 22) have caused a great deal of concern and may not be as reliable as the corresponding data for the baseline testing. All of the solutions prepared from the outlet solids as well as certain control samples analyzed at the same time by ICP (for example, the filter from a blank train) showed high concentrations of many of the metals, but particularly four: chromium, manganese, molybdenum, and nickel. Apparently there was widespread contamination or interference from a source not normally encountered, but there is no information as to the identity of the source. Extensive back-up analyses with the graphite furnace were performed to eliminate errors in the ICP data, and repeated ICP analyses were made in a final effort to obtain the most dependable data set possible. Nevertheless, the suspicion remains that outlet front-half concentrations of several of the metals in the low-NO_x testing were not as high as are reported. Unfortunately, the exact reason for such an error cannot be stated, and thus recommendation for avoidance of future problems cannot be offered.

Table 23 gives values of the ratios of trace element amounts to the total particulate mass at the ESP inlet and outlet. These values are the element totals (from front and back halves of the sampling train) divided by the amount of particulate matter in the front half. The ratios do not indicate in all cases the element concentration in the solid since a substantial part of the element must have occurred in the vapor state. For selenium in particular, the very large ratio at the ESP outlet in either test series reflects occurrence of this element as a vapor. For most of the elements, however, the ratio was higher at the ESP outlet than at the ESP inlet. (Admittedly, ratios at the outlet in many instances had to be reported as limits; even though numerical values are not known always, the limits still convey the impression of high ratios at the outlet). The observation of widespread high ratios of elements to total particulate matter would appear to indicate that few of the elements occurred as matrix elements in the fly ash and that most occurred predominantly as fine particles or surface components of fine particles. Barium is the clearest exception. This could imply that most of the elements existed as vapors at some time in their thermal history, even if not during the sampling process.

Two important questions to be answered from the data in Tables 21 and 22 are as follows: 1) How did operation of the cold-side ESP influence passage of the trace elements to the outlet? 2) How did the degree of penetration through the ESP system change when the switch was made from baseline boiler operation to low-NO_x operation? Answers to these questions may be seen more easily from the summary given in Table 24. This table gives data on penetrations of the individual elements through the two tandem ESPs as percentages of the inlet amounts. Specifically, the table shows outlet concentrations as percentages of inlet concentrations. It does this for each test series, baseline or low-NO_x, two ways: for the one test in which the cold-side ESP was in operation, and for the three tests in which only the hot-side ESP was in operation (an average penetration value is given in the latter case).

Consider the question of whether the cold-side ESP lowered the penetration of any element in either test series. First, if the uncertainties in the data are duly taken into account, only a few instances of lower penetrations with the cold-side ESP in operation can be noted. Selenium in both test series and arsenic in the low-NO_x series were more completely removed from the gas stream with the cold-side ESP operating. The actual data for selenium, failing to show distribution reliably between the particulate and vapor states, make a very poor case for a reduced penetration due to the cold-side ESP. The data for arsenic, on the other hand, are not subject to this equivocation, and reduced penetration stands as a possible real phenomenon. Finally, however, a different perspective needs to be considered. The cold-side ESP can only improve the removal of particulate matter as a primary function. If the elements that clearly occur primarily as particulate matter (the majority) are considered, no significant improvement in removal is evident.

Now consider the question of whether the emission of the trace elements was improved or degraded after low-NO_x firing was adopted. If the data obtained with the hot-side ESP operating alone are considered, the changes in emissions of elements showing changes upon adoption of low-NO_x firing differences in the two test series are as follows: arsenic (+), barium (+), cobalt (-), copper (-), manganese (+), nickel (-), phosphorus (+), selenium (-), and vanadium (+). There is no consistent pattern for these elements, most of which occur in the particulate matter subject to control in an ESP. Consequently, the effect of changing the firing conditions is obscure. Nevertheless, low-NO_x firing apparently made no dramatic increase in penetrations.

Concentrations of speciated elements. Three elements were determined in different chemical forms: mercury, chromium, and arsenic. The results of speciation work on these elements is described in the following paragraphs.

(a) Mercury. Tables 25 and 26 present the results of efforts to speciate mercury by use of the sampling train devised by Nicolas Bloom of Brooks Rand, Ltd. A probe packing of quartz wool collects particulate matter. Behind the filter, two sorption tubes packed with KCl-treated soda lime collect methylmercury and vapors of Hg(II), and two tubes packed with iodated carbon collect the vapor of Hg(0) — that is, elemental mercury — which passes through the soda lime tubes without being trapped. Hg(II) compounds are likely to include the chloride $HgCl_2$, which has been identified in the combustion gases from some types of sources that have both mercury and chlorine in the fuel (11).

The more complete and successful sampling and analysis were completed during the baseline test series. The results of this work are presented in Table 25; the data consist of mercury concentrations at the ESP inlet and outlet. Both particulate and gas phases were analyzed at the inlet. As expected, there was little mercury found in the inlet particulate matter; the total ranged from 0.023 to 0.343 $\mu g/Nm^3$, and methylmercury was undetectable at the 0.0002-$\mu g/Nm^3$ level. There was no methylmercury detectable in the inlet gas phase at the concentration 0.0001 $\mu g/Nm^3$, but Hg(II) and Hg(0) were found in concentrations totalling 4-6 $\mu g/Nm^3$.

The results at the ESP outlet showed that the total gas-phase mercury concentration ranged from 6.40 to 10.05 $\mu g/Nm^3$, somewhat higher than the inlet range of 3.91 to 6.39 $\mu g/Nm^3$. Mercury obviously was not created in the flue gas stream during passage through the ESP system;

probably, the outlet data are the more reliable because of the lesser likelihood of interference during the sampling operation. (The high-temperature gas sampled at the ESP inlet may have raised the temperature of the traps in the sampling apparatus to levels that caused incomplete adsorption of mercury. Alternatively, the heavy concentration of particulate matter at the inlet may have impeded sample flow.) The proportions of the three vapor forms of mercury at the outlet were approximately as follows: methylmercury, 0.02%; Hg(II), 80%; and Hg(0), 20%. No attempt was made to analyze the particulate matter at the ESP outlet, which was present in very small amounts and was unlikely to contain much mercury.

The data for the low-NO_x test series, given in Table 26, show vapor compositions at the ESP outlet that were similar to those found at the ESP inlet. The concentration of methylmercury, however, was somewhat higher at the outlet; it represented no less than 0.2% of the total in any one sample and as much as 0.9% in two samples. The ratio of Hg(II) to Hg(0) was somewhat higher than before.

Previous reports of $HgCl_2$ in combustion gases have dealt with the incineration of municipal wastes, where the concentrations of mercury and chlorine (as HCl) are substantially higher than they are in the combustion gases from coal. Certainly, higher concentrations of HCl would promote the conversion of elemental mercury to $HgCl_2$. Even with only a modest chlorine level in the coal at Site 110 (0.15-0.20%), however, the concentrations of HCl expected are high enough, according to thermodynamics, to make $HgCl_2$ the predominant vapor form of mercury. The analytical reports given in Appendix C temper somewhat the certainty of the identification of Hg(II)-containing vapors in the flue gas at Site 110; they state that there is the possibility of the conversion of Hg(0) to Hg(II) in the sampling train. In the absence of knowledge that this transformation could have actually occurred, however, the prudent conclusion from the information known is that Hg(II) was probable as the dominant form of mercury.

(b) Chromium. Table 27 presents the results of determinations of Cr(VI) in the ash samples from the front half of the metals train. For the samples from the baseline testing, around 5% of the total chromium was found as Cr(VI) in the extracts of the ESP inlet samples and much higher percentages — up to 76% or perhaps an even higher value — were found as Cr(VI) in the outlet samples. For the samples from the low-NO_x testing, lesser amounts of the total chromium was identified as extracted Cr(VI). For the inlet samples at low-NO_x conditions, 1-2% of the total chromium was thus identified; for the corresponding outlet samples, Cr(VI) was always below the detection limit but accounted for no more than 35% of total chromium. An increasing ratio of Cr(VI) to total chromium on moving from the ESP inlet to the ESP outlet, as suggested by the baseline data, is logical because the particle size of the ash decreases from the inlet to the outlet of the ESP and the fraction of total chromium that is extractable would be likely to increase also. The percentage of the total chromium that is actually Cr(VI) may not change, but it may appear to change simply because more is extracted (the particles are smaller and more of the total chromium is exposed to extraction).

(c) Arsenic. Table 28 gives the results on the speciation of arsenic. In the inlet samples from the baseline testing, an average of 0.40% of the total arsenic was extracted as As(III) and 29.3% was extracted as As(V). In the inlet samples from the low-NO_x testing, the results were so highly variable that a clear-cut summary is difficult to make. Nevertheless, the extracted arsenic was clearly As(V) in the main. In the outlet samples from the baseline testing, both As(III) and As(V) in the extract increased absolutely over values at the inlet, and both increased as percentages of the total. Also, the ratio of As(III) to As(V) increased. Paradoxically, the extracted As(V) appeared to exceed the total arsenic. In the second set of outlet samples, the quantities of As(III) were highly variable and often below the limit of detection; the quantities of As(V) were substantially higher and averaged approximately 18.9% of the total arsenic.

Several features of the data on arsenic require comment, as follows:

- The values of total arsenic concentration for both the inlet and outlet samples differ substantially between the baseline and low-NO_x samples. The data for the baseline samples probably are more accurate. Difficulty was encountered in the analysis of the samples from both locations in the low-NO_x test series, as mentioned previously in this report. There is, however, no objective reason for considering one data set to be more nearly accurate than the other.

- The paradox mentioned above, wherein the extracted amount of arsenic exceeded the total present, arises only because two different portions of the sample were analyzed for total arsenic and for the separate species. The processing of the two portions differed considerably. The portion that yielded the value for total arsenic was subjected to acid digestion before the analysis was made, whereas the portion used for speciation was simply extracted in water. Perhaps in the acid digestion and the following analysis part of the arsenic was lost, or part was not converted to AsH_3 for determination by the hydride AAS method, or some other error was made in the analysis.

Table 21
Trace Element Concentrations ($\mu g/Nm^3$) at the ESP Inlet and Outlet under Baseline Conditions[a,b,c]

		Sept. 18, 1991		Sept. 19, 1991		Sept. 20, 1991		Sept. 21, 1991	
		Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
As	F	134	1.39	192	2.31	218	2.12	237	0.49
	B	0.47	0.11	0.34	0.39	0.78	<7	0.41	0.45
	T	134	1.50	192	2.70	218	≥2.12	237	0.94
Ba	F	1075	5.6	2369	4.8	2340	4.7	2633	5.2
	B	6.2	<1	<1	1.1	<1	<14	<1	1.0
	T	1083	≥5.6	2369	5.9	2340	≥4.7	2633	6.2
Be	F	66.5	<0.6	38.2	<0.7	68.2	<0.7	70.0	<0.7
	B	<0.5	<0.6	<0.6	<0.7	<0.5	<0.7	<0.6	<0.7
	T	66.5	<1.2	38.2	<1.4	68.2	<1.4	70.0	<1.4
Cd	F	99.0	<1.2	1323	<1.3	140	1.7	139	1.4
	B	768[d]	<1.2	1.12	1.2	1.1	<2.0	<1	<1.2
	T	867	<2.4	1324	≥1.2	140	≥1.7	139	≥1.4
Co	F	138	<6	211	<7	167	<7	174	<7
	B	<5	<6	<6	20	<5	1.3	<5	<7
	T	138	<12	211	≥20	167	>1.3	174	<14
Cr	F	826	4.6	1048	10.7	1116	10.4	1110	19.5
	B	2.8	6.6	2.40	2.6	1.28	5.2	1.41	11.7
	T	829	11.2	1050	13.3	1117	15.6	1111	31.2
Cu	F	440	5.3	341	5.0	566	6.1	498	7.7
	B	<1	<1	<1	<1	<1	5.6	<1	25.4
	T	440	≥5.3	340	≥5.0	567	11.7	498	33.1
Hg[e]	F	0.68	0.02	0.51	0.02	0.50	0.03	0.82	<0.02
	B	1.04	0.55	1.43	0.36	0.62	0.61	3.99	1.45
	T	1.72	0.57	1.94	0.38	1.12	0.64	4.81	≥1.45
Mn[f]	F	428	5.7	1434	7.6	1394	8.7	1521	5.5
	B	26.3	15.8	498	2670.9	341	70.7	533	106.2
	T	454	21.5	1932	2677.5	1735	79.4	2054	111.7
Mo	F	626	<6	758	<7	524	<7	689	11.6
	B	<5	<6	<6	66	<5	<7	<5	<6
	T	626	<12	758	≥66	524	<14	689	≥11.6

Table 21 (Concluded)
Trace Element Concentrations (μg/Nm^3) at the ESP Inlet and Outlet under Baseline Conditions[a,b,c]

		Sept. 18, 1991		Sept. 19, 1991		Sept. 20, 1991		Sept. 21, 1991	
		Inlet	Outlet[b]	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
Ni	F	552	<6	743	10.4	788	<7	736	7.9
	B	<5	<6	<6	12.1	<5	3.6	<5	6.0
	T	552	<12	743	22.5	788	≥3.6	736	13.9
P	F	1247	<12	1296	<13	965	<14	1289	<14
	B	<10	<12	<11	<13	<11	<14	<10	<14
	T	1247	<24	1296	<26	965	<28	1289	<28
Pb	F	882	<12	1250	<7	1421	8.2	1293	14.9
	B	<10	7.6	<1	55	<5	<1	<5	<6
	T	882	≥7.6	1250	≥55	1421	≥8.2	1293	≥14.9
Sb	F	100	<12	161	<13	132	<14	117	<14
	B	<10	<12	<11	<13	<10	<7	<10	<14
	T	100	<24	161	<26	132	<21	117	<28
Se	F	16.3	14.2	37.6	3.3	19.5	32.0	30.5	27.0
	B	6.9	37.9	5.0	78.0	20.2	37.0	16.5	25.5
	T	23.2	52.1	42.6	81.3	39.7	69.0	47.0	52.5
V	F	3943	9.8	4171	<1.3	3288	21.9	4216	32.9
	B	<1	<1	<1	<1.3	<1	<1	<1	<1
	T	3943	≥9.8	4171	<2.6	3288	≥21.9	4216	≥32.9
Volume, Nm^3		1.594	1.611	1.569	1.525	1.684	1.405	1.686	1.446

[a] All of the data presented here were obtained by the methods of ICP, HGAAS, GFAAS, and CVAAS for samples obtained with the Multiple Metals Train.

[b] The cold-side ESP operated only on September 18.

[c] F refers to the front half of the sampling train (up to and including the filter). B refers to the back half—that is, impingers. T gives the sum or total of both F and B. Gas volumes sampled are denoted at the bottom of the table.

[d] This value as an obvious outlier that is to be disregarded.

[e] These data for Hg are regarded as unreliable in comparison with results from the sorption-tube measurements.

[f] High Mn concentrations in outlet impingers are attributable to $KMnO_4$ transfer by splashing from the $KMnO_4$ impingers to the H_2O_2 impingers.

Table 22
Trace Element Concentrations (μg/Nm^3) at the ESP Inlet and Outlet under Low-NO$_x$ Conditions[a,b,c]

		Jan. 14, 1992		Jan. 15, 1992		Jan. 16, 1992		Jan. 17, 1992	
		Inlet	Outlet[b]	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
As	F	80.8	7.3	102	16.1	67.6	19.8	103	8.3
	B	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
	T	80.8	≥7.3	102	≥16.1	67.6	≥19.5	103	≥8.3
Ba	F	7100	16.4	6840	21.2	8580	31.6	6390	30.5
	B	<10	<10	<10	<10	<10	<10	<10	<10
	T	7100	≥16.4	6840	≥21.2	8580	≥31.6	6390	≥30.5
Be	F	65.4	<0.8	69.7	<0.8	53.3	<0.8	61.3	<0.8
	B	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	T	65.4	<1.3	69.7	<1.3	53.3	<1.3	61.3	<1.3
Cd	F	70.4	5.9	387	<2.0	66.4	<2.0	139	<2.0
	B	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
	T	70.4	≥5.9	387	<4.0	66.4	<4.0	139	<4.0
Co[d]	F	205	4.35	183	4.04	184	4.11	178	3.65
	B	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	T	205	4.35	183	4.04	184	4.11	178	3.65
Cr	F	1230	40.5	729	29.2	776	30.8	1140	17.0
	B	223[e]	35.3	3.0	3.0	2.2	3.3	2.8	3.2
	T	1453	75.8	732	32.2	778	34.1	1143	20.2
Cu	F	532	<0.8	330	<1.5	442	<1.5	590	<1.5
	B	4.5	5.6	2.7	14.8	3.1	<4.0	3.7	<4.0
	T	536	≥5.6	333	14.8	445	<5.5	594	<5.5
Hg[f]	F	2.22	<0.40	1.71	<0.40	1.30	<0.40	0.81	0.49
	B	1.33	2.14	0.09	0.15	0.06	0.13	0.36	0.98
	T	3.55	2.14	1.80	0.15	1.36	≥0.13	1.17	1.47
Mn[d]	F	1510	20.8	1030	13.4	1730	15.6	1230	13.6
	B	2.3	13.8	17.7	4.3	1.7	0.5	8.5	1.9
	T	1512	34.6	1048	17.7	1732	16.1	1240	15.5
Mo[d]	F	982	46.3	713	45.7	910	54.6	1120	10.5
	B	3.4	4.7	2.7	3.7	<3.0	<1.0	<3.0	<0.5
	T	985	51.0	716	49.4	910	54.6	1120	10.5

Table 22 (Concluded)
Trace Element Concentrations ($\mu g/Nm^3$) at the ESP Inlet and Outlet under Low-NO_x Conditions[a,b,c]

		Jan. 14, 1992		Jan. 15, 1992		Jan. 16, 1992		Jan. 17, 1992	
		Inlet	Outlet[b]	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
Ni	F	813	17.4	706	<7.5	780	<7.5	679	<7.5
	B	<3.0	<3.0	1.4	<3.7	<3.0	<3.0	<3.0	<3.0
	T	813	17.4	707	<11.2	780	<10	679	<10
P	F	819	60.4	1920	72.7	679	69.0	950	69.1
	B	<10	<10	<10	<10	<10	<10	<10	<10
	T	819	60.4	1920	72.7	679	69.0	950	69.1
Pb[d]	F	866	1.94	605	9.12	531	53.9	776	28.9
	B	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	T	866	1.94	605	9.12	531	53.9	776	28.9
Sb	F	42.6	<3.0	130	<3.0	--	<3.0	720	<3.0
	B	<2.0	14.7	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
	T	42.6	14.7	130	<5.0	--	<5.0	720	<5.0
Se	F	137	18.2	112	50.4	143	27.6	115	48.8
	B	55.6	75.4	106	136	1.0	160	108	156
	T	193	93.6	218	186	144.0	188	223	205
V	F	4790	39.9	4050	40.9	5460	55.7	5130	64.7
	B	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
	T	4790	39.9	4050	40.9	5460	55.7	5130	64.7
Volume, Nm^3		1.959	1.269	1.942	1.338	1.881	1.397	2.001	1.432

[a] All of the data presented here were obtained by the methods of ICP, HGAAS, GFAAS, and CVAAS for samples obtained with the Multiple Metals Train.

[b] The cold-side ESP operated only on January 14.

[c] F refers to the front half of the sampling train (up to and including the filter). B refers to the back half—that is, impingers. T gives the sum or total of both F and B. Gas volumes sampled are denoted at the bottom of the table.

[d] Data for Co, Mn, Mo, and Pb in the outlet front halves are based on a reanalysis of digestates, which showed evidence of unrealistic high concentrations of these elements when the digestates were first analyzed.

[e] These data for Hg are regarded as unreliable in comparison with results from the sorption-tube measurements.

[f] High Mn concentrations in outlet impingers are attributable to $KMnO_4$ transfer by splashing from the $KMnO_4$ impingers to the H_2O_2 impingers.

Table 23
Trace Element Quantities as Ratios to the Mass of Total Particulate Matter (μg/g) at the ESP Inlet and Outlet[a]

	Baseline testing		Low-NO$_x$ testing	
	Inlet	Outlet	Inlet	Outlet
As	26.6	49.1	11.8	≥100
Ba	284	156	938	≥265
Be	8.4	<33	8.2	<19
Cd	89.4	35.8	11.9	<53
Co	23.7	<420	24.5	59.6
Cr	140	456	140	642
Cu	63.4	339	62.2	<110
Hg	0.32	19.2	0.25	>15
Mn	206	–	177	325
Mo	90.0	<300	122	625
Ni	96.6	<400	97	<184
P	166	<800	149	982
Pb	165	616	90.9	328
Sb	17.6	<700	42.6	<120
Se	5.16	1700	25.9	2360
V	540	<400	632	725

[a] The data are based on all observations in four tests in the two test series.

[b] Differences between the inlet data here and the inlet data in the next-to-the-last column of Table 16 or 17 are due to the fact that here both front and back halves of the metals train are considered whereas there only the front half is considered.

Table 24
Penetration of Trace Elements Through the ESP System
(percentages of inlet concentrations observed at the outlet)

	Baseline testing, Sept. 1991		Low-NO_x testing, Jan. 1992	
	Cold-side ESP on[a]	Cold-side ESP off[a]	Cold-side ESP on[a]	Cold-side ESP off[a]
As	1.1	0.93	9.0	>18
Ba	≥0.52	ca 0.23	≥0.23	≥1.3
Be	<1.8	<2.6	<2.0	<2.0
Cd	<0.28	≥0.77	≥8.4	<3.3
Co	<8.7	ca 6.1	2.1	2.2
Cr	1.3	≥1.8	5.22	3.52
Cu	≥1.2	3.4	≥1.0	ca 2.0
Hg[b]	--	--	--	--
Mn	1.3	0.4[c]	3.0	1.1
Mo	<1.9	ca 4.0	4.7	4.4
Ni	<2	1.8	2.1	<1.5
P	1.9	<2.0	7.4	7.07
Pb	≥0.86	≥2.0	0.2	5.1
Sb	<24	<19	34.5	2.27
Se	Indeterminate[d]	Indeterminate[d]	48.5	Indeterminate[d]
V	≥0.25	ca 0.51	0.83	1.10

[a] Cold-side ESP operated on September 18 and January 14 only.

[b] Penetration of Hg judged to be close to 100% in view of vapor concentrations found at the outlet with the sorption collectors (see Table 25).

[c] Mn found in back half of outlet train was disregarded because of evident contamination of the peroxide impingers with liquid from the permanganate impingers.

[d] Se at the outlet often exceeded that measured at the inlet.

Table 25
Mercury Speciation Data for Flue Gas in Baseline Testing
(concentrations in $\mu g/Nm^3$)

ESP inlet	Sept. 18[a]	Sept. 19	Sept. 20	Sept. 21
Particulate				
methylmercury	<0.002	<0.002	<0.002	<0.002
total	0.343	0.101	0.027	0.023
Gas phase				
methylmercury	<0.0001	–	<0.0001	<0.0001
Hg(II)	1.92	ND	5.00	0.90
Hg(0)	1.65	ND	1.37	3.95
total	3.57	ND	6.37	4.85
Grand total	3.91	ND	6.39	4.87

ESP outlet	Sept. 18[a]	Sept. 19	Sept. 20	Sept. 21
Particulate	ND	ND	ND	ND
Gas phase				
methylmercury	0.0009	0.0026	0.0020	0.0017
Hg(II)	5.66	5.53	8.51	8.07
Hg(0)	0.74	2.52	1.54	1.50
total	6.40	8.05	10.05	9.57
Grand total[b]	6.40	8.05	10.05	9.57

[a] The data here are a combination of results for September 17 and September 18, when the cold-side ESP operated.

[b] The contribution of the particulate forms (unmeasured) is presumed to be negligible.

ND=not determined.

Table 26
Mercury Speciation Data for Flue Gas in Low-NO_x Testing
(concentrations in $\mu g/Nm^3$)

	Jan. 14[a]	Jan. 15	Jan. 16	Jan. 17
ESP inlet				
total	<0.003	ND	ND	<0.03[b]
ESP outlet				
Particulate	0.02	0.04	0.04	<0.001
Gas phase				
methylmercury	0.057	0.012	0.016	0.075
Hg(II)	5.78	6.57	3.70	8.11
Hg(0)	0.68	0.65	0.45	0.75
Grand total	6.53	7.27[c]	4.21	8.94

[a] The cold-side ESP operated only on January 14.

[b] This was the only occasion when an attempt was made to speciate the inlet mercury.
The results were: methyl, 0.024
Hg(II), <0.01
Hg(0), <0.008

[c] Another result, when only iodated carbon was used for sorption, was 4.45.

Table 27
Chromium Speciation Data for Flue Gas Solids (collected on filters)

Type of testing	Date of sample	ESP inlet			ESP outlet		
		Total Cr, μg/g	Cr (VI), μg/g	%	Total Cr, μg/g	Cr (VI), μg/g	%
Baseline	9/18	131	5.6	4.3	–	–	–
	9/19	146	9.5	6.5	330	251	76
	9/20	148	7.7	5.2	227	<360	<160
	9/21	137	9.7	7.1	462	140	30
Low NO_x	1/14	143	<10	<7	524	<10	<2
	1/15	108	1.6	1.5	408	<93	<23
	1/16	89	1.6	1.8	503	<105	<21
	1/17	164	2.7	1.6	259	<89	<35

Table 28
Arsenic Speciation Data for Flue Gas Solids
(collected on filters)

Type of testing	Date of sample	ESP inlet			ESP outlet		
		Total As, μg/g	Extracted As, μg/g		Total As, μg/g	Extracted As, μg/g	
			As (III)	As (V)		As (III)	As (V)
Baseline	9/18	21.3	0.113	3.79	41.4	14.6	54.5
	9/19	27.1	0.073	10.8	71.3	51.2	84.2
	9/20	28.9	0.143	7.73	46.3	25.3	48.9
	9/21	29.3	0.097	8.86	11.6	ND	ND
avg.[a]		26.6	0.106	7.80	53.0	30.4	62.5
avg, %[b]		100.0	0.40	29.3	100.0	57.4	117.9
avg, %[c]		–	1.3	98.7	–	32.7	67.2
Low NO_x	1/14	9.4	<0.030	0.445	136	<5.8	47.1
	1/15	15.0	0.564	0.340	330	11.7	28.1
	1/16	7.8	<0.032	12.1	292	<4.2	54.3
	1/17	14.9	0.213	13.5	125	7.7	36.1
avg.[a]		11.8	<0.210	6.6	221	<7.4	41.4
avg, %[b]		100.0	<1.8	56	100.0	<3.4	18.9
avg, %[c]		–	<3.0	>97	–	<15	>85

[a] Average of data on the three or four lines above.
[b] Percentage of total arsenic.
[c] Percentage of extracted arsenic.

5.4.2 Individual Flue Gases

Data on concentrations of individual components of the flue gas at the ESP inlet and outlet are presented in Table 29. These data give an overall perspective on the compositions of the flue gas; they do not, however, include all of the results of the Institute's measurements, which are also presented in later tables. Some of the data in Table 29 are from the project CEMs; these data are averages of readings at 5-min intervals for the duration of each day of sampling. The balance of the data consists of SO_2 and SO_3 concentrations from the Institute's controlled condensation train (CCT), O_2 and CO_2 concentrations from the Teledyne and Fyrite measurement devices, and H_2O concentrations calculated from amounts of moisture collected on Drierite adsorbent or collected as condensates. All of the data are for the dry basis at actual O_2 concentrations except that the data for H_2O vapor are for the wet basis.

One issue of high interest that can be addressed from the data in Table 29 is the effect that the boiler modifications had on the NO_x concentration. The two CEMs measured somewhat differently. One instrument indicated that the outlet NO_x concentration decreased from about 380 ppm to about 236 ppm (each calculated for 4% O_2) as the result of boiler modifications; the other CEM indicated a change approximately from 365 to 250 ppm (again, calculated for 4% O_2). The first indicated change is a reduction of 38%, whereas the latter is a reduction of 32%. The data here are not necessarily a typical measure of the reduction of NO_x emissions brought about by the low-NO_x burner changes, but they are recorded to show the effect evident during the measurement program described in this report. The ultimate conclusion at Site 110 about low-NO_x combustion is that a 45% reduction in NO_x formation occurred at full load but that a decreasing improvement occurred at reduced load (ultimately at 40% of full load, no improvement was seen.)

The data on CO and THC (total hydrocarbon) can also be examined to reveal effects of the burner modifications. Paradoxically, the average CO concentration during the low-NO_x test series was lower than that during the baseline testing. The data on THC during either test series were not consistent enough to show what effect, if any, the burner modification had on hydrocarbons. (Other data given later in Section 5.4.4 indicate that the concentration of total hydrocarbon, if referred to in the broadest possible context, cannot be as low as the data in Table 29 suggest). Specifically, the apparent concentrations of benzene ranged up to

10,000 $\mu g/Nm^3$, which is the same as 3 ppmv. This discrepancy will be discussed further in Section 5.4.4.)

Another matter of interest is the increase in O_2 across the two ESPs. The nominal value was 4% at the inlet or 6-8% at the outlet. At least semi-quantitatively, the data on SO_2 and CO_2 reflect the inleakage of air within the ESPs and air heater that was responsible for the increase in O_2 concentration. To compensate for the effects of air inleakage on gas concentrations, concentrations of varying substances in the gas streams were adjusted to the values that would have occurred at 4% O_2, the nominal concentration at the ESP inlet.

Approximately 25 ppm of SO_3 was found at the ESP inlet. This represented somewhat more than 1% of the total concentration of sulfur oxides. This relative concentration of SO_3 was not unexpected, but it is higher than Institute investigators have usually encountered. Only about 12 ppm of SO_3 (actually present at the lower outlet temperature as H_2SO_4) was found at the outlet. The loss between the inlet and the outlet is due to the adsorption of acid vapor on the fly ash particles as the temperature decreases from 700 to 300 °F and probably due also, to some extent, to the condensation of acid vapor on the surfaces of the air heater, which in places were below the dewpoint of the acid vapor (roughly 280-290 °F).

Further details on the concentrations of SO_2, all expressed for 4% O_2, are presented in Table 30. The several ways of expressing concentrations of SO_2 in this table are as follows:

- The concentration of sulfur in the coal was used to calculate the concentration of SO_2 to be expected in the flue gas, assuming that all of the sulfur was to be found in the flue gas (that is, negligible amounts were found in pyrite waste, bottom ash, or fly ash).

- The concentrations of SO_2 from the controlled condensation train were adjusted to 4% O_2 and reported as percentages of the concentrations predicted from the coal composition.

- The quantities of SO_2 apparent from the amounts of sulfate found in the Acid Gases Train were expressed as the equivalent concentrations of SO_2 at 4% O_2 in the flue gas and as percentages of the values expected from the coal composition.

Recoveries of SO_2 were more consistent for samples collected with the controlled condensation train. The average recoveries based on samples from this train were 86% at the ESP inlet and 90% at the outlet. There is little evidence from this investigation that the much longer sampling time for the Acid Gases Train is justified for SO_2. Typical gas volumes with this train, around 0.5 Nm^3, yielded about 5 g of sulfate from SO_2, which is far greater than that required for accurate quantitation. (Later, experience with Acid Gases Train has yielded far more consistent data on SO_2 than Table 30 reveals.)

Concentrations of HF and HCl calculated from the coal compositions and the analysis of samples from the Acid Gases Train are presented in Table 31. Recoveries of HF were more erratic than those of HCl; recoveries of either gas were more erratic at the ESP inlet than at the ESP outlet. The best indication of the degree to which fluorine and chlorine in the coal were to be found in the gas phase is obtained from the data for the ESP outlet. The average HF recovery at the outlet was 80%; the average HCl recovery at the outlet was 109%.

An upper limit for the concentration of the vapor H_3PO_4 was calculated from the results of the ion chromatographic determinations of chloride and sulfate. Phosphate ion was in no case observed; if it had been observed, the threshold quantity in the solution would have been about 2500 μg. This solution contained dissolved gases from about 0.5 Nm^3 of flue gas. Hence, the upper limit for H_3PO_4 vapor would have been 1 ppmv. (Calculation of the phosphate vapor as H_3PO_4 is arbitrary; the limit as P_2O_5 would have been 0.5 ppmv.)

During the baseline measurements, ammonia was found at the inlet of the ESP at concentrations ranging from 0.7 to 3.1 ppmv and at the outlet at concentration ranging from 0.7 to 1.5 ppmv. During the low-NO_x measurements, on the other hand, ammonia was not present except possibly at concentrations below 0.3 ppmv. These measurements were based on data taken with the ammonia-responsive electrode; all of the ammonia found was in the condenser, where it presumably had reacted with SO_3, which was in excess, to produce ammonium sulfate.

The Institute investigators were very skeptical about the occurrence of ammonia in gases from a conventionally-fired pulverized-coal boiler but cannot disregard the results because of confirmation from other observations. White deposits were observed in the filter chamber of the Modified Method 5 train (for semi-volatile organics), behind the filter, as though some material that passed through the filter as a gas or gases condensed on the clean gas side of the filter due to further cooling. Scrapings of this material for infrared analysis were identified as ammonium sulfate. Moreover, a water rinse of the deposit was analyzed for ammonia and sulfate and found to contain them in the mole ratio equivalent to ammonium sulfate.

There is no explanation for the absence of detectable amounts of ammonia with low-NO_x firing of the boiler. Logically, an enhancement of ammonia formation with less efficient oxidation might have been expected.

During the baseline testing, cyanide ion was collected in impingers containing a buffer solution of carbonate and bicarbonate behind a particulate filter. The amounts of cyanide found corresponded to HCN concentrations of 0.4 ppmv at the ESP inlet or 0.3 ppmv at the ESP outlet. During the low-NO_x testing, cyanide was collected in the carbonate/bicarbonate buffer of the Acid Gases Train (used with peroxide omitted, to avoid oxidation of the cyanide). Calculated concentrations of HCN in the flue gas at the ESP inlet were 0.05-0.06 ppmv or at the outlet 0.04-0.05 ppmv. There was a clear-cut decrease during the second series of tests, in opposition to the change anticipated from low-NO_x firing.

Table 29
Concentrations of Various Flue Gas

		September 1991				January 1992			
Component	Method	9/18	9/19	9/20	9/21	1/14	1/15	1/16	1/17
Inlet:									
O_2, %	Teledyne	3.8	4.0	4.1	3.8	4.0	3.8	4.4	3.9
	OT711A	2.42	2.70	2.90	3.04	3.60	3.44	3.81	3.83
	OT711B	3.54	3.90	4.24	4.25	4.32	4.27	4.46	4.77
	OT721A	2.88	3.34	3.45	3.70	3.28	3.32	3.46	3.50
	OT721B	4.33	4.85	4.92	4.85	3.56	3.83	3.57	3.3
SO_2, ppmv	CCT	2204	2142	2243	2147	1936	2050	1859	20387
SO_3, ppmv	CCT	24	26	29	26	26	22	28	26
CO_2, %	Fyrite	14.3	14.0	14.0	14.5	13.6	14.9	13.5	14.0
H_2O, %	Drierite	–	–	–	–	7.0	7.6	6.0	6.3
	Condensate	10.2	10.3	9.3	9.7	8.9	8.7	8.9	8.7
	Condensate	–	10.9	9.3	9.3	8.8	7.9	8.0	7.5
Outlet:									
O_2, %	Teledyne	6.2	7.6	8.0	8.8	7.0	7.5	7.5	7.5
	AT790	6.13	6.40	6.62	6.66	6.17	6.31	6.39	6.36
	AT791	4.45	4.78	5.12	5.13	5.25	5.33	5.39	5.37
SO_2, ppmv	CCT	1794	1787	1751	1724	1594	1552	1510	1537
	AT790	1961	1955	1930	1870	1912	1968	1929	1939
	AT791	2034	1892	1752	1792	1387	1751	1729	1743
	XXX					1587	1766	1797	1789
SO_3, ppmv	CCT	12	13	12	13	10	11	10	12
NO_x, ppmv	AT790	323	328	334	332	209	203	200	201
	AT791	388	309	344	341	226	232	230	235
	XXX					180	180	187	187
CO_2, %	Fyrite	12.5	11.0	12.0	11.5	11.5	11.5	11.5	12.0
CO, ppmv	AT790	8.94	10.6	12.1	13.2	11.1	3.34	10.7	0.67
THC, ppmv	TT790	0.49	0.45	–	–	0.82	0.31	0.37	0.44
H_2O, %	Condensate	9.7	9.6	9.5	9.4	8.2	7.5	7.4	6.9
	Condensate	9.0	9.3	8.1	9.2	6.7	6.7	5.8	6.5

Note: the prefaces OT, AT, and TT designate plant CEM data as does the symbol XXX for still other CEM data.

Table 30
Concentrations of SO_2 at 4% O_2

Source of data	SO_2 concentrations, ppmv							
	September 1991				January 1992			
	9/18	9/19	9/20	9/21	1/14	1/15	1/16	1/17
Coal composition	2420	2520	2490	2280	2290	2370	2350	2360
CCT train, inlet (% recovery)	2180 (91)	2140 (86)	2260 (90)	2120 (92)	1940 (84)	2030 (84)	1900 (83)	2030 (84)
CCT, outlet (% recovery)	2060 (86)	2270 (91)	2290 (92)	2400 (105)	1940 (84)	1960 (82)	2340 (102)	1940 (81)
AGT, inlet (% recovery)	2200 (92)	4040 (162)	1650 (66)	1490 (65)	-- (--)	1360 (57)	2140 (93)	2260 (94)
AGT, outlet (% recovery)	2720 (113)	2220 (89)	2410 (96)	3020 (131)	1460 (63)	2030 (85)	2490 (108)	2000 (83)

CCT = Controlled Condensation Train
AGT = Acid Gases Train

Table 31
Concentrations of HF and HCl at 4% O_2

Source of data	Gas	Gas concentration, ppmv							
		September 1991				January 1992			
		9/18	9/19	9/20	9/21	1/14	1/15	1/16	1/17
Coal composition	HF	10.2	10.3	8.9	10.4	7.8	7.3	7.8	8.7
	HCl	143	129	145	142	119	119	133	133
AGT, inlet									
Concentration	HF	0.4	1.8	6.7	5.7	0.5	4.9	7.4	7.0
(% recovery)	HF	(4)	(17)	(75)	(55)	(7)	(66)	(94)	(80)
Concentration	HCl	10.5	162	95	78	14	129	230	70
(% recovery)	HCl	(7)	(125)	(66)	(55)	(12)	(108)	(173)	(53)
AGT, outlet									
Concentration	HF	10.3	8.7	6.7	5.7	5.7	5.4	7.1	7.6
(% recovery)	HF	(101)	(85)	(75)	(55)	(73)	(74)	(91)	(88)
Concentration	HCl	100	162	163	120	150	142	157	152
(% recovery)	HCl	(70)	(125)	(112)	(84)	(128)	(119)	(118)	(114)

AGT = Acid Gases Train.

5.4.3 Aldehydes and Ketones

Analytical objectives. The single compound of primary interest was formaldehyde. The method used for collecting and determining formaldehyde, however, is applicable to other aldehydes and to certain ketones. Aldehydes such as acetaldehyde and propionaldehyde could have been detected but were not; formaldehyde was the only aldehyde detected. Acetone was the only ketone detected.

The reason that a wide variety of aldehydes and ketones is subject to inclusion in the analysis is that any carbonyl compound that reacts with 2,4-dinitrophenylhydrazine to produce the corresponding hydrazone is subject to detection. These hydrazone derivatives are exceptionally stable and allow the compounds of interest to be removed quantitatively from the gas stream being sampled; they also aid in detection and quantitation in the laboratory.

From the point of volatility, any of the carbonyl compounds listed above is a volatile organic compound. Formaldehyde was not detected among the compounds identified in samples from the VOST procedure, as shown in Section 5.4.4 to follow; acetone was identified, on the other hand, in the VOST samples, but this compound is presumed to have been present largely an analytical artifact at the concentrations found in the VOST samples. The reason why formaldehyde was detected when collected in DNPH solution but not in the sampling components of the VOST is not known; it is likely, however, to have been the result of the high degree of solubility of formaldehyde in the water condensate of VOST and the inefficient stripping of the compound from the condensate during the analytical procedure.

Analytical results. The analysis of samples from the baseline test series proved to be faulty. The analyst failed to extract the analytes from the aqueous collection medium and thus failed to concentrate the analytes for determination in methanol solution. Nevertheless, the analyst reported acetone present in each sample but reported none of the aldehydes. The results for acetone were clearly flawed because of the presence of this compound at high concentrations even in the blanks used for control purposes. The aldehydes were reported to be below certain very low stated limits; however, none of the aldehydes could have had detection limits as low as those given. In actuality, the aldehydes could have been present at significant concentrations —

specifically, at the levels found for formaldehyde in the samples from the low-NO_x series described below.

The data from the second test series are presented in Table 32. The data include concentrations for the two compounds detected (formaldehyde and acetone), which are corrections from the concentrations apparent in the raw data. The footnote of the table lists the average background concentrations derived for blank solutions of DNPH; these background concentrations were subtracted from the original apparent concentrations of the two analytes in the samples.

Although the data are variable, they indicate rather strongly that formaldehyde was present at a lower concentration at the ESP outlet than at the inlet. This is an anomalous result for a compound that is certain to be present in the vapor state and thus not subject to removal by electrostatic precipitation. Conceivably, the diminished concentration at the outlet is the result of chemical transformations proceeding in the gas phase between the inlet and the outlet. Oxidation is one possible process, with either O_2 or NO_x serving as the reactant. Ozone in the corona regions is another possible reactant.

The concentrations of formaldehyde in Table 32 range from 10 to 163 $\mu g/Nm^3$. The equivalent concentrations on the volume basis are 8-130 ppbv.

The highest concentration of acetone listed in Table 32 is about 20 $\mu g/Nm^3$, which is equivalent to 8 ppbv. The magnitude of the acetone concentrations in this table seems to confirm the interpretation of the results for acetone in the section to follow, to the effect that apparent concentrations as high as 20,000 $\mu g/Nm^3$ from VOST are the result of field or laboratory contamination of the samples.

Table 32
Concentrations of Formaldehyde and Acetone in the Low-NO$_x$ Test Series

Sample date	Sample location	Concentration, μg/Nm^3	
		Formaldehyde	Acetone
1/14/92	Inlet	76	4
	Outlet	10	18
1/15/92	Inlet	159	22
	Outlet	10	2
1/16/92	Inlet	21	8
	Outlet	11	1
1/17/92	Inlet	163	1
	Outlet	11	1

Blank corrections already applied: formaldehyde, 4.9 μg
acetone, 5.6 μg

5.4.4 Volatile Organic Compounds

5.4.4.1 Analytical Objectives. The first task was to determine whether two specific compounds, benzene and toluene, were present and to determine the concentrations of these two compounds. These compounds are the primary targets of concern in the class of compounds known as volatile organics. This statement is based on the draft report prepared by Radian Corporation as a guide to the sampling and analysis of air toxics in EPRI's FCEM program (7). The two compounds are also among those named in Title III of the Clean Air Act Amendments of 1990.

The second task was to determine whether any other identifiable volatile compounds that would be collected by the same sampling method might be present. To complete this task, use was made of a list of target compounds that had been compiled from compounds named in SW-846 Method 8240, which is the method employed during this project for the analysis of volatile organics. This list of compounds includes benzene and toluene. The list is used routinely by the GC/MS laboratory at Southern Research for identification and quantitation of substances that are analyzed by Method 8240 in appropriate quantities, having detection limits of the order of a few nanograms for most compounds.

The list of target compounds employed in the analysis of samples obtained during the baseline test series is given in Table 33. There are a total of 41 compounds on the list. Of this number, 35 are actual target compounds to be identified if present in the sample. Among the 35 are 24 compounds that appear in the Clean Air Act Amendments; these compounds are identified in the table. In addition to the 35 compounds, there are 3 surrogates and 3 internal standards, which are defined below. The table also gives the limits of detection of the compounds. These limits are concentrations in the gas sampled; they are derived from the inherent sensitivity of the analytical method and an assumed gas volume of 0.02 Nm^3. This is the maximum volume found practical at the ESP inlet; the detection limits are thus minimum values for the inlet and will be higher if a lesser volume of gas is taken. The maximum sample volume at the outlet, on the other hand, was 0.04 Nm^3 and thus the detection limit of each compound at the outlet was half of the value listed in the table.

The list of compounds employed in the analysis of samples from the low-NO_x series was essentially the same. It differed in that methyl iodide took the place of carbon disulfide and in that 2-chloroethyl vinyl ether was omitted. Carbon disulfide remained detectable in the low-NO_x series as a "tentatively identified compound," as defined below. Methyl iodide was added as the result of an effort to augment the list of target compounds by including others from the 189 in Title III of the 1990 Clean Air Act Amendments. The list of surrogates for the low-NO_x samples differed in that 4-bromofluorobenzene was not used as a surrogate when Tenax or Tenax/charcoal sorption tubes were analyzed, since the recovery of this compound from these media had been found very erratic.

The definition of surrogates and internal standards is as follows:

1) A surrogate is a compound not to be expected in the source sampled which is added to a sample in the original collection medium just before the sample is processed in the laboratory for analysis. Two of the surrogates are deuterated compounds, which makes them absent from the samples collected in the field; the third compound is a halogenated derivative of benzene that also is not to be expected to occur naturally (this is bromofluorobenzene, BFB, the surrogate not used in the low-NO_x samples with Tenax or Tenax/charcoal). A surrogate is added to each of the three sampling media (Tenax, Tenax/charcoal, and water vapor condensate) before laboratory processing (transfer of the collected volatile compounds from the original collection medium to an intermediate sorption tube, just ahead of gas chromatographic processing). The completeness of recovery of each surrogate therefore provides an inferential means of assessing the completeness of recovery of unknowns from the source sampled.

2) An internal standard is a compound added to each fraction of the sample just before the fraction is injected onto the chromatographic column. The internal standards are distinguishable from unknowns in the source stream for the same reasons that the surrogates are distinguishable.

The final analytical task with respect to volatiles was to attempt to identify compounds that were detected but not identified in the group of target compounds listed in Table 33. Unknown compounds that are subjected to identification attempts produce signals that are at least 10% of the signals from adjacent internal standards in the ion-current chromatograms. If an unknown compound is to be included in efforts at attempted identification, it obviously fails to satisfy criteria of identification as one of the target compounds. Its mass spectrum is compared against a library of mass spectra in a computer program. Compounds in the library that bear sufficient similarity to the unknown are termed "hits"; the degree of similarity is rated numerically. The experience on this project was that a high degree of matching was rarely achieved and most of the compounds remained simply unknowns, rather than "tentatively identified compounds," a term that implies a reasonably successful attempt at identification.

5.4.4.2 Illustrative Chromatograms. Chromatograms illustrating the results obtained in the analysis of VOST samples are presented in Figures 8 and 9. (These chromatograms are for two components from the experiment designated later in Table 36 as 9/19/91 Inlet Run 1). The chromatogram in Figure 8 is for one 40-mL portion of water vapor condensate; the chromatogram in Figure 9 is for the Tenax sorption tube.

The peaks for surrogates and internal standards are identified by the code entered in each figure. The relative peak heights and areas can be appreciated by the following information of the concentrations and masses of these compounds. In the condensate, the concentration of each surrogate was in the range 38-45 ng/mL; comparison of each concentration value in this range with the original value, 50 ng/mL, reflects the extent of recovery during the analysis. The concentration of each internal standard in the condensate was the same original value, 50 ng/mL. From the Tenax, the mass of each surrogate recovered varied more widely; compared with the original amount of each surrogate (250 ng), the mass of 1,2-dichloroethane-d4 (SURR 1) was 25.6 ng (10.2%), that of toluene-d8 (SURR 2) was 261 (104.4%), and that of 4-dibromobenzene (SURR 3) was 7.36 ng (7.4%). In the Tenax sample, the mass of each internal standard was 250 ng.

In addition to the peaks of the surrogates and internal standards, the peaks, concentrations, and masses of certain identified and unidentified compounds can be pointed out.

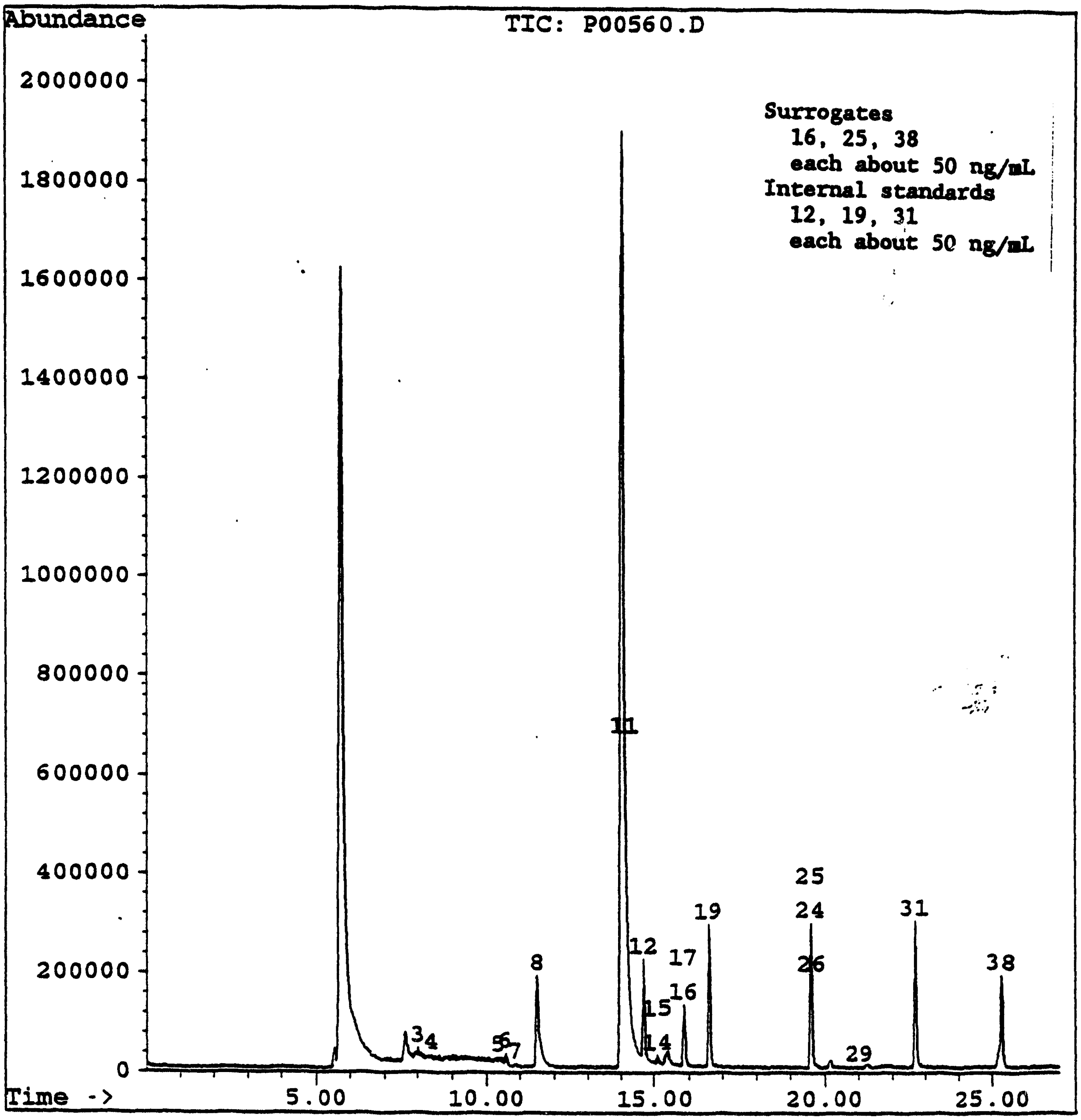


Figure 8. Ion chromatogram of volatiles from water vapor condensate.

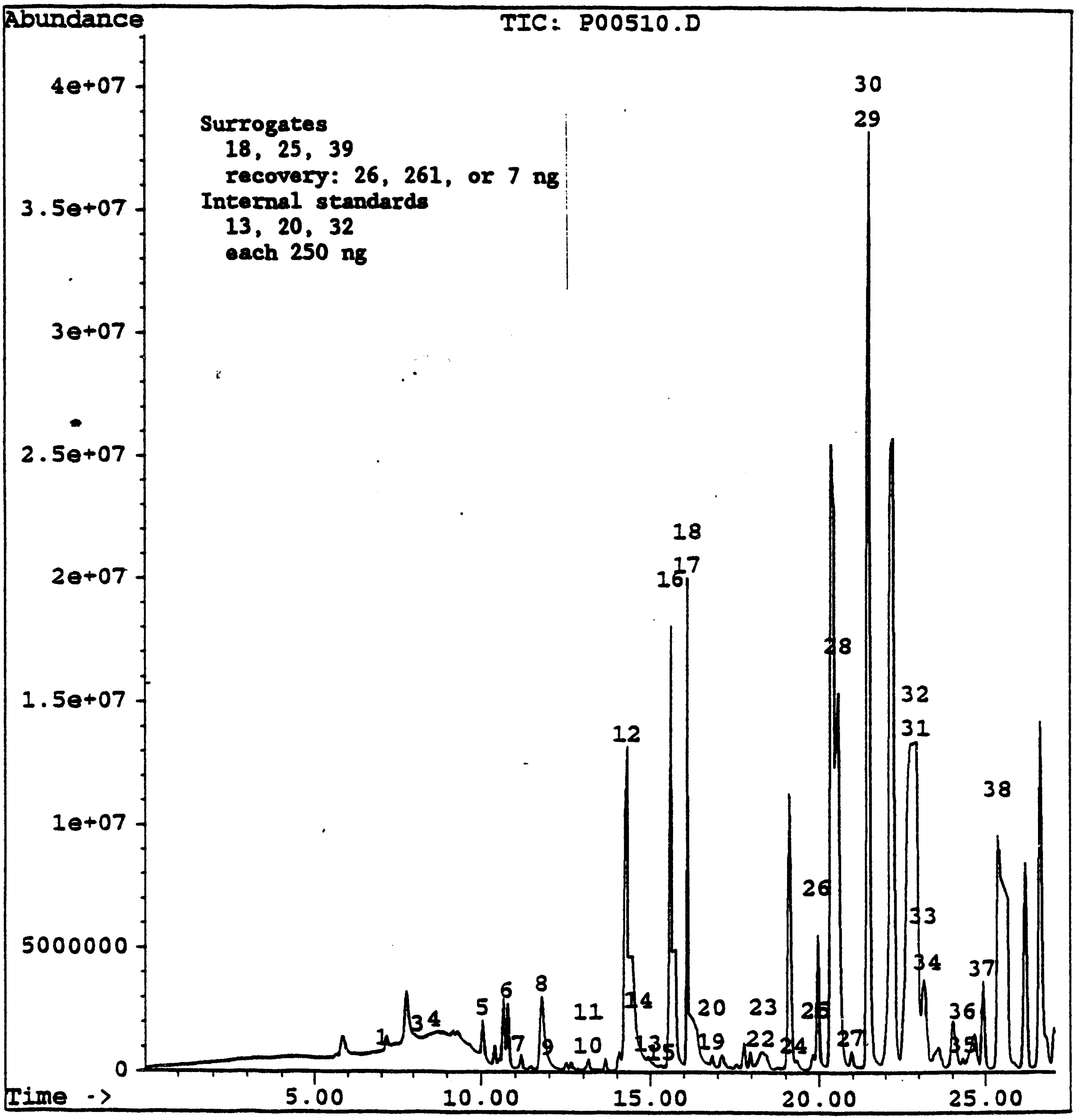


Figure 9. Ion chromatogram of volatiles from Tenax sorption tube.

Information on these matters is given in Table 34. The two compounds of primary interest, benzene and toluene, are relatively insignificant in the chromatogram for the condensate; moreover, the two compounds at the highest concentrations in the condensate are not identified. Benzene and toluene are relatively more important in the sample from Tenax, but acetone (believed to be an external contaminant) is dominant and three unknowns are also important.

5.4.4.3 Target Compounds – Identities and Concentrations. The compounds from the list of target compounds in Table 33 that were identified are listed in Table 35. The maximum concentration of each compound that was observed in each test series, baseline or low-NO_x, is listed with regard to the sampling location, ESP inlet or outlet. Many of the compounds were not observed at all in some of the samples. Thus, the concentrations listed in Table 35 are not meant to be representative of the test results. They are meant simply to show the diversity of concentrations observed. The fact that the concentrations are given in the unit $\mu g/Nm^3$ is underscored because the magnitudes of the numbers are so large compared to the magnitudes for most of the other types of analytes discussed in this report.

The data in Table 35 for the baseline testing came from samples collected in 2- or 10-min intervals at the ESP inlet, or 2-, 5-, or 40-min intervals at the outlet. The data for the low-NO_x series came from samples collected during intervals of 2-, 5-, or 10-min intervals at either location. The 40-min samples from the ESP inlet during the first test series were so heavily loaded that they could not be analyzed; moreover, they heavily contaminated the analytical system and caused serious inconvenience and delay in restoring the operation of the analytical system. This problem with the baseline samples led to avoidance of 40-min sampling intervals during the low-NO_x sampling.

Several important observations can be made from the information in Table 35, as follows:

- The list of compounds identified is far longer for the baseline samples than for the low-NO_x samples. Moreover, there was only one compound found in the latter samples that was not present in the baseline samples. This exception was methyl iodide, which was added to the target list after the baseline work was completed. There was the suspicion that irreversible contamination of the analytical system from

40-min inlet samples from the baseline test series contributed to the results with volatiles during the subsequent analyses of the remainder of the samples from that series. A new and thus uncontaminated GC column was used for the second set of samples.

- Concentrations of some compounds reached astounding levels. For example, acetone was found at concentrations as high as 20,000 $\mu g/Nm^3$, which is equivalent to 8 ppmv. Concentrations of benzene reached very high levels also, as high as 10,000 $\mu g/Nm^3$, which is equivalent to 3 ppmv.

- Some of the compounds identified can be logically eliminated as components of the flue gas streams sampled and attributed to contamination of the samples either in the field or in the laboratory. For some compounds this statement is speculation; for others, there is a fair technical basis. There was the suspicion that acetone was a field contaminant during the baseline sampling; there were then steps taken during the low-NO_x sampling to eliminate the contamination. All work-up of the volatiles sampling train was performed in a dedicated, solvent-free enclosure and, as a consequence, no acetone contamination occurred. The appearance of 1,1,1-trichloroethane in every sample was almost certainly due to laboratory contamination because of the appearance of this compound in laboratory and field blanks. Some compounds surely must be regarded as contaminants because they appeared, in some cases, only once at very high concentrations; examples of compounds for which this was true were the ketones 2-butanone, 2-hexanone, and 4-methyl-2-pentanone.

- Although Table 35 does not list concentrations with respect to sampling location, ESP inlet or outlet, an examination of the data in detail makes it difficult to say whether or not samples from the two locations systematically ranked differently in the concentrations observed. Some compounds had their maximum concentrations at the inlet; others were seen at the highest levels at the outlet. The absence of any difference between inlet and outlet concentrations would appear logical for a compound in the vapor state; hence, the occurrence of maximum concentrations randomly at the inlet or the outlet might be expected if there were uncontrolled factors responsible for variations.

Benzene and related aromatics in the baseline testing. It is appropriate to focus attention on the concentrations found for benzene and toluene, because these were prominent target compounds. It is also appropriate to consider at the same time certain related aromatic hydrocarbons — the xylenes, ethylbenzene, and styrene. The similarity of these compounds is indicated as follows:

- Benzene has the unsubstituted aromatic ring.
- Toluene has one methyl substituent.
- Each xylene has two methyl substituents — ortho, meta, or para.
- Ethylbenzene has one ethyl substituent.
- Styrene has one vinyl substituent ($CH_2=CH$-).

Details of the data for the aromatic hydrocarbons from the baseline testing are presented in Table 36. Concentrations of each compound in the gas stream that was sampled are given in two columns; the first is based on the amount found in the Tenax sorption tube, and the second is based on the amount found in the Tenax/charcoal sorption tube. Occasionally, a small amount was found in the water condensate, but the amount was always small enough, relatively speaking, to be disregarded. The two columns of data are presented to show whether the second sorption tube contained a large amount compared with the first, which would suggest that breakthrough occurred and thus the total found in both tubes was probably less than the true amount present. Evidence of breakthrough occurred only occasionally; hence, evidence of breakthrough does not often invalidate the sum of the two concentrations as representative of the actual duct concentration.

The lines of data for samples labeled FB ("field blank") provide another way to evaluate the reliability of the concentration data. As subsequently described in Appendix D.4, a field blank is a sorption tube that has had no air or flue gas drawn through it. The numerical values for the blanks are placed within parentheses to designate that these values are given in the mass unit ng, not the concentration unit μg/Nm^3 or the equivalent concentration unit ng/L. When the concentrations equivalent to the mass in the field blank are calculated and compared with the raw concentration values, the magnitudes of the corrections are usually insignificant. For example, for the 9/19/91 inlet values, the corrections are of the order of 6-8%.

There were a few experiments that yielded results that can be presumed to be erroneous. One was Run 3 for the outlet on 9/18/91, where the Tenax tube yielded no benzene during the analysis. Another that raises doubt is Run 2 for the inlet on 9/17/91, where the indicated concentrations of benzene and toluene are unusually high. One curious aspect of the data that may be noteworthy is found in the two sets of results where five runs are listed in each set: the calculated concentration of benzene appeared to increase as the sample volume decreased. A possible explanation for this anomaly is that part of the benzene found may have been due to a partial degradation of the Tenax resin (2,6-diphenylene oxide polymer) that was caused by some factor other than the duration of sampling, perhaps the presence of a reactive flue gas component.

The very large amounts of benzene often observed were beyond the range of the usual calibration of the method for this compound. The calibration was usually assumed to be linear to several times the maximum amount of benzene used in calibration. An inquiry into the validity of the extrapolations indicated that the extrapolations were essentially valid, although they may have given values for benzene that were 20% below the true values.

Clearly, the concentrations of toluene were much below those of benzene and those of the other related aromatic hydrocarbons were even lower and were not consistently high enough to be observed.

Benzene and related aromatics in the low-NO$_x$ testing. Details of the analytical data for the volatile aromatic hydrocarbons from the low-NO$_x$ testing are presented in Table 37. The calculated gas-phase concentrations from the low-NO$_x$ work are generally lower than those from the baseline testing. As might be expected, the comparison of Tenax and Tenax/charcoal at lower indicated concentrations shows no evidence of breakthrough during sampling. The amounts of the compounds found in the field blanks (FB) were all zero and cause no correction (they are not listed). The samples collected during the low-NO_x work include those labeled AB ("air blank"), which were obtained by sampling outdoor air on the platforms adjacent to the sampling ports. The air blanks, unlike the field blanks, did reveal measurable amounts of the hydrocarbons on occasion but not amounts large enough to cause significant correction.

Benzene and related aromatics from an overall perspective. No comment on the possible effect of the cold-side ESP on the concentrations of benzene and the related aromatics seems appropriate since only one set of inlet and outlet samples was obtained with the cold-side ESP in operation. Moreover, the variability of the data would seem to make it hopeless to attempt to discern the subtle effect, if any, of the cold-side ESP. If the operation of this ESP is eliminated as a relevant variable, then the data for benzene and the other compounds can be shown in relationship to variables that clearly are relevant: sampling time, sampling location, and test occasion.

The data for benzene and toluene are shown in relationship to these variables in Table 38 (the data for the xylenes, ethylbenzene, and styrene are omitted from this summary, since these compounds appeared to be significant only in the baseline test series). For each test series, each sampling time, and each sampling location, the average concentrations of benzene and toluene are shown, as well as the standard deviation if two or more results are represented. Despite the high degree of variability of the data, as indicated by standard deviations that are as large as the averages in several instances, certain observations that appear important can be made:

- Changing the combustion process to reduce the emissions of NO_x apparently did not increase the emission of the aromatic hydrocarbons as the result of less efficient combustion of the coal. If the data address this issue at all, they say that the emission of the aromatics was reduced, not elevated. This may not be a credible conclusion, however, because of the uncertain quality of the data.

- Despite indications that there were differences on occasion between inlet and outlet concentrations, the prudent conclusion is that no clear difference is illustrated. A striking indication of a difference is seen in comparing the inlet and outlet benzene concentrations from the low-NO_x test series. Surely, however, benzene was not generated in the ESP system, although such a phenomena appears to have occurred if the data are taken at face value.

- Trends in increasing apparent concentration as the sampling time was shortened are evident, as mentioned before. The phenomenon that caused this anomaly may have been a more or less constant quantity of an analyte, contributed by an unknown source, that made an exaggerated impact on short-term samples.

- The credibility of benzene and toluene concentrations at the levels listed in Table 38 will have to be assessed in terms of the data obtained from other PISCES investigations. These data from other studies are not available to the Institute investigators. They are certainly far higher than the ranges reported recently by Garcia for coal-burning plants in Europe (12), where benzene concentrations, for example, were 20 $\mu g/Nm^3$.

5.4.4.4 Unidentified Compounds. Table 34 notes unidentified compounds that were evident in two of the chromatograms. The mass spectrum of each unknown was compared with mass spectra in the reference library but no reasonable match was obtained. The first-listed unknown in the condensate had its principal ion at Mass 44 and had no other ion of any corresponding significance; yet, the compound was not identified. Obviously, CO_2 is a candidate to account for Mass 44, but it is not a probable candidate for the observed retention of 5.75 min. The other unknown in the condensate had its principal ion at Mass 75 and had other minor ions near Mass 45; still, no match with the mass spectrum of a known compound was obtained. On the scale whereby the quality of a match against a known compound is rated numerically, the quality of matches for these two unknowns was zero; no candidate compound as a match was named.

The first unknown listed in Table 34 for the Tenax sample was the same as the first in the condensate. The other two were different; the second unknown had its primary ion at Mass 89 and its secondary ion at Mass 59; the third unknown had its primary ion at Mass 163 and its secondary ion at Mass 133. The quality of matches against mass spectra of known compounds was zero for all three unknowns.

The Tenax sample referred to above had not just three but a total of twelve compounds that were not target compounds. Not any one of the twelve could be matched against library compounds, and the highest quality of any attempted match was 50 (on a scale from 0 to 100).

Some of the information given above dealt with identified target compounds in regard to relative concentrations at the ESP inlet and outlet and in regard to relative concentrations in the baseline and low-NO_x test series. Further information can be compiled on the matter of unidentified compounds in each of these contexts; even though the compounds cannot be named, the extent to which they are found may be regarded as a key to the performance of the ESP system or the boiler. Table 39 gives a summary on a pair of experiments at the ESP inlet and outlet in the baseline test series and another corresponding pair of experiments in the low-NO_x test series. The most striking feature of the data in this table is that the numbers and concentrations of unidentified compounds were far greater in the baseline tests than in the low-NO_x tests. Differences between the ESP inlet and the ESP outlet, on the other hand, were not remarkable in either test series. The data on unidentified compounds, therefore, seem to be in accord with the data on identified target compounds (notably benzene and toluene) with respect to two important observations:

- Concentrations of volatile compounds were not changed to an important degree as the result of passage of the gas stream through the ESP system.

- Concentrations of volatile compounds were higher under the baseline operating conditions than under low-NO_x conditions.

Table 33
Target Compounds in VOST Samples
(list includes surrogates and internal standards)

Compound[a]	Detection limit, $\mu g/Nm^3$
✓ 1. chloromethane	0.12
✓ 2. vinyl chloride	0.16
✓ 3. bromomethane	0.43
✓ 4. chloroethane	1.89
5. 1,1-dichloroethene	0.06
6. acetone	2.46
✓ 7. carbon disulfide	0.15
✓ 8. methylene chloride	0.29
9. 1,1-dichloroethane	0.09
10. trans-1,2-dichloroethene	0.05
11. 2-butanone	1.26
12. bromochloromethane IS1	–
✓ 13. chloroform	0.11
14. 1,1,1-trichloroethane	0.43
✓ 15. carbon tetrachloride	0.11
✓ 16. benzene	0.06
✓ 17. 1,2-dichloroethane-d_4 SURR1	–
✓ 18. 1,2-dichloroethane	0.13
19. 1,4-difluorobenzene IS2	–
✓ 20. trichloroethene	0.08
21. 1,2-dichloropropane	0.12
22. bromodichloromethane	0.12
✓ 23. cis-1,3-dichloropropene	0.05
24. 2-hexanone	0.17
25. toluene-d_8 SURR2	–

Table 33 (Concluded)
Target Compounds in VOST Samples
(list includes surrogates and internal standards)

Compound[a]	Detection limit, $\mu g/Nm^3$
✓ 26. toluene	0.06
27. 2-chloroethyl vinyl ether	0.06
✓ 28. trans-1,3-dichloropropene	0.09
✓ 29. 1,1,2-trichloroethane	0.11
✓ 30. tetrachloroethene	0.06
31. 4-methyl-2-pentanone	0.29
32. dibromochloromethane	0.10
33. chlorobenzene-d_5 IS3	--
✓ 34. chlorobenzene	0.03
✓ 35. ethylbenzene	0.07
✓ 36. m- & p-xylene	0.08
✓ 37. o-xylene	0.03
✓ 38. styrene	0.06
✓ 39. bromoform	0.05
40. 4-bromofluorobenzene SURR3	--
✓ 41. 1,1,2,2-tetrachloroethane	0.13

[a] The check mark designates a compound listed in Title III of the Clean Air Amendments Act of 1990.

Table 34
Compounds Represented in the Chromatograms in Figures 8 and 9

Compound	Retention time, min	Peak number	Concentration or mass
Condensate			
unknown	5.8	none	590 ng/mL
acetone	10.5	6	62
methylene chloride	11.6	8	40
unknown	14.0	11	674
benzene	15.8	17	1.2
toluene	19.6	26	0.2
Tenax			
unknown	5.8	none	620 ng
acetone	10.7	6	23,000
unknown	11.8	8	1213
benzene	16.0	17	8380
unknown	19.1	24	2891
toluene	20.0	26	3020

Table 35
Compounds Detected in VOST Samples

Compound	Maximum concentration, $\mu g/Nm^3$, observed[a]	
	Baseline samples	Low-NO_x samples[b]
chloromethane	330	–
bromomethane	6	100
chloroethane	60	–
acetone	20,000	–
carbon disulfide/methyl iodide[c]	200	18
methylene chloride	1100	860
2-butanone	3900	–
1,1,1-trichloroethane	900	370
carbon tetrachloride	26	–
benzene	10,000	1600
2-hexanone	160	–
toluene	4300	15
4-methyl-2-pentanone	370	–
chlorobenzene	60	–
ethylbenzene	870	1.6
m- & p-xylene	80	14
o-xylene	170	4.3
styrene	2800	–
1,1,2,2-tetrachloroethane	6	–

[a] NOTE: It is clear that some of these results, especially for the baseline, reveal contamination and should be accepted with strong reservations, as explained in the text. Acetone in the baseline result is an example of such contamination.

[b] Blank means the compound was not detected.

[c] Carbon disulfide is reported for baseline samples and methyl iodide for low-NO_x samples.

Table 36
Volatile Aromatic Hydrocarbons Observed During Baseline Testing

(concentrations are in $\mu g/Nm^3$ = ng/L; masses in parentheses, for field blanks, are in ng)
(T = Tenax; T/C = Tenax/charcoal)

Date, location	Run	Time, min	Vol., L	Benzene		Toluene		Xylenes		Ethylbenzene		Styrene	
				T	T/C	T	T/C	T	T/C	T	T/C	T	T/C
9/17/91 Inlet[a]	1	10	4.75	1780	2380	103	11.5	0.3	0.9	2.0	0.3	0	0
	2	2	1.16	9740	270	4280	0	244	0	168	0	2810	0
	FB	-	-	(112)	(241)	(5.7)	(17)	(0)	(1.2)	(0)	(0)	(0)	(0)
9/18/91 Outlet[a]	1	40	16.1	570	11.2	63.4	0.04	3.1	0	10.0	0	29.2	0
	2	40	15.4	460	117	35.5	0.9	2.0	0.5	3.7	0.3	12.3	0.3
	3	40	15.7	0	21.0	15.7	0.4	0.2	0.4	0	0	1.2	0
	4	10	3.92	1910	42.9	19.9	2.3	4.9	0	3.8	0	65.3	0
	5	2	0.69	4480	134	52.0	45.8	15.5	2.6	868	0	156	0
	FB	-	-	(55)	(92)	(3.8)	(5.6)	(0)	(0.4)	(0)	(0)	(0)	(0)
9/19/91 Inlet	1	10	4.55	1840	745	664	21.8	15.4	0.6	0	0.9	92.1	12.4
	FB	-	-	(506)	(257)	(25.8)	(15.2)	(0.7)	(0.4)	(0)	(0)	(11.6)	(5.8)
9/19/91 Outlet	1	40	14.8	628	8.6	6.2	2.0	1.0	0.3	0.2	0	0	0
	2	40	14.8	617	26.6	6.4	0.5	0.2	0.1	0.5	0.1	0.7	0
	3	40	14.7	455	10.1	9.3	0.2	0.1	0.1	0.5	0.1	1.0	0.3
	4	10	3.71	1940	39.9	2.5	0.3	5.0	0.5	0.7	0	0.8	0
	5	2	1.21	2450	31.1	3.2	0	14.8	0	2.0	0	3.1	0
	FB	-	-	(0)	(0)	(11.4)	(1.2)	(1.6)	(0.2)	(1.0)	(0)	(0)	(0)
9/20/91 Inlet	1	10	4.45	1550	59.1	134	4.0	14.1	1.9	7.2	0.9	24.9	0
	FB	-	-	(92)	(98)	(11.4)	(7.7)	(2.8)	(0.2)	(0.2)	(0)	(0)	(0)
9/20/91 Outlet	1	40	14.2	639	66.7	10	0.3	4.4	0.6	2.2	0.3	7.8	0
	2	40	17.6	470	73.3	6.4	0.5	3.5	0.1	1.5	0	17.1	0

[a] The cold-side ESP operated on both 9/17/91 and 9/18/91 but not on the other dates. One latter day was the regular test day for most purposes with the cold-side unit on; the first day, however, provided samples that were not available on the second day.

Table 37
Volatile Aromatic Hydrocarbons Observed During Low-NO_x Testing
(concentrations are in $\mu g/Nm^3$ = ng/L)

Date, location	Run	Time, min	Vol., L	Benzene		Toluene		Xylenes		Ethylbenzene		Styrene	
				T	T/C	T	T/C	T	T/C	T	T/C	T	T/C
1/14/92 Inlet[a]	1	10	5.51	490	6.0	3.4	0.9	0	0.4	0	0	10.4	0
	2	5	2.87	146	7.0	2.9	0	2.5	0	0	0	0	0
	3	2	0.87	310	0	12.1	0	6.0	0	0	0	0	0
1/14/92 Outlet[a]	1	10	4.14	1530	26.1	9.5	1.4	11.9	0	0	0	0	0
	2	10	4.27	860	3.9	3.6	2.9	2.3	0	0	0	0	0
	3	5	2.15	1080	6.8	3.9	0	0	0	0	0	0	0
	4	5	2.12	1010	8.5	5.2	5.8	0	0	0	0	0	0
	5	2	0.74	766	15.5	12.8	2.5	11.1	2.5	0	0	0	0
	6	2	0.64	1110	28.1	12.9	0	12.9	0	0	0	0	0
	AB	10	4.22	50.9	0	3.8	0	0	0	0	0	0	0
1/15/92 Inlet	1	10	5.71	1200	3.8	10.5	0	0	0	1.6	0	12.8	0
	2	5	2.76	643	0	0	0	0	0	0	0	0	0
	3	2	1.24	644	0	0	0	0	0	0	0	0	0
	AB	10	5.45	9.4	0	0	0	0	0	0	0	0	0
1/15/92 Outlet	1	10	4.49	486	1.6	3.1	0	0	0	0	0	0	0
	2	5	2.14	468	8.6	4.7	0	0	0	0	0	0	0
	3	2	0.89	508	0	6.0	0	4.3	0	0	0	0	0
	AB	10	4.40	55	0	2.6	0	0	0	0	0	0	0

Table 37 (Concluded)
Volatile Aromatic Hydrocarbons Observed During Low-NO_x Testing
(concentrations are in $\mu g/Nm^3$ = ng/L)

Date, location	Run	Time, min	Vol., L	Benzene		Toluene		Xylenes		Ethylbenzene		Styrene	
				T	T/C	T	T/C	T	T/C	T	T/C	T	T/C
1/16/92 Inlet	1	10	5.50	83	0	7.3	0	0.6	0	0.6	0	22.4	0
	2	5	2.68	113	0	4.9	0	0	0	0	0	0	0
	3	2	1.13	237	0	0	0	0	0	0	0	0	0
	AB	10	5.35	0	0	0	0	0	0	0	0	0	0
1/16/92 Outlet	1	10	4.40	1110	13.4	3.5	1.1	1.2	0	0	0	0	0
	2	5	2.11	1290	3.8	4.4	0	3.3	0	0	0	0	0
	3	2	0.94	1570	26.9	0	0	3.0	0	0	0	0	0
	AB	10	4.39	239	0	0	0	0	0	0	0	0	0
1/17/92 Inlet	1	10	5.31	64.4	0	6.4	0	0	0	0	0	14.3	0
	2	5	2.78	29.1	0	0	0	0	0	0	0	0	0
	3	2	1.11	31.1	0	0	0	0	0	0	0	0	0
	AB	10	5.23	8.6	0	0	0	0	0	0	0	0	0
1/17/92 Outlet	1	10	4.38	1400	0	0	0	1.0	0	0	0	0	0
	2	5	2.11	2100	8.3	4.6	0	2.1	0	0	0	0	0
	3	2	0.73	5200	25.6	0	0	4.3	0	0	0	0	0
	AB	10	4.25	377	0	2.1	0	0	0	0	0	0	0

[a] The cold-side ESP operated only on 1/14/92.

Table 38
Average Concentrations and Standard Deviations for Benzene and Toluene

Test series	Sampling time, min	Benzene		Toluene	
		Inlet	Outlet	Inlet	Outlet
Baseline	40	–	500 ± 200	–	20 ± 20
	10	2800 ± 1300	1980 ± 20	310 ± 320	13 ± 14
	2	10,000	3500 ± 1500	4300	50 ± 67
Low NO_x	10	160 ± 220	1090 ± 430	7.1 ± 2.6	6.6 ± 3.4
	5	230 ± 280	1200 ± 590	2.4 ± 2.3	5.7 ± 3.0
	2	310 ± 260	1850 ± 1930	3.0 ± 6.0	6.8 ± 7.1

Table 39
Summary of Information on Unidentified Volatile Compounds

Test series[a]	Sample location	Number of unknowns	Concentration range, $\mu g/Nm^3$, individual cpds.	Concentration total, $\mu g/Nm^3$, all cpds.
Baseline	Inlet			
	Condensate	2	1400-11,200	12,600
	Tenax	12	7-810	3000
	Tenax/charcoal	10	130-2750	7700
				23,300
Baseline	Outlet			
	Condensate	2	2500-21,700	24,200
	Tenax	7	150-2000	4500
	Tenax/charcoal	6	100-700	10,200
				38,900
Low NO_x	Inlet			
	Condensate	0	0	0
	Tenax	4	10-70	740
	Tenax/charcoal	3	20-230	470
				1210
Low NO_x	Outlet			
	Condensate	0	0	0
	Tenax	4	13-90	170
	Tenax/charcoal	3	22-290	590
				760

[a] Sampling experiments identified in Table 36 as 9/19/91 Inlet Run 1 and Outlet Run 4 and in Table 37 as 1/16/92 Inlet Run 1 and Outlet Run 1.

5.4.5 Semi-Volatile Organic Compounds

5.4.5.1 Analytical Objectives. The analytical objectives with semi-volatile organic compounds were similar to those previously described with volatile compounds:

- To determine whether the samples from the gas ducts contained any compound on a list applicable specifically to the PISCES program

- To determine whether the samples contained any compound from an extended list of target compounds routinely used in the GC/MS laboratory at Southern Research

- To attempt to identify non-target compounds that were found to be present.

The 16 polynuclear aromatic hydrocarbons listed in Table 40 comprised the fundamental target list of semi-volatile organics to be determined in the samples from the gas ducts. This list of compounds was taken from the draft report prepared by Radian Corporation as a guide to the sampling and analysis of air toxics in the PISCES program (7). Additional compounds were added to this list by Radian at a later time; some but not all of these compounds are included in the expanded list of target compounds described below.

The expanded list of target semi-volatile organics is given in Table 41. This list was compiled from the compounds named in EPA Method 8270 (for the analysis of semi-volatiles by capillary column technique); it is a list of 79 compounds that the GC/MS laboratory at Southern Research is programmed to identify and quantify. (Compound numbers in the table run up through 80; however, three compound numbers — 6, 12, and 22 — are not assigned. Also, as will be explained, 12 of the 79 compounds are actually on the list as control compounds, not as compounds to be identified.) In addition to the compound names, the table lists the detection limits for the compounds. These limits are based on the detection limits in the extract analyzed, the volume to which the extract is finally reduced by evaporation, and the volume of gas sampled. The specific limits given in the table are based on a final extract volume of 1 mL and a gas volume of 2 Nm^3 (the minimum for any of the samples analyzed).

The expanded compound list in Table 41 includes all of the 16 PAHs from Table 40. The list also includes 20 compounds from Title III of the Clean Air Act Amendments of 1990 (none of which are on the PISCES list in Table 40). Finally, the list includes 12 compounds referred to as surrogates and internal standards (there are 6 compounds in each group and each is identified in the table). As with the analysis of volatile organics, a surrogate is a compound not to be expected in the source sampled; some of the surrogates are deuterated, for example, and the others are halogenated compounds not frequently encountered. Each surrogate is added to XAD resin from the sampling train before extraction is started. Again, as with the analysis of volatile organics, an internal standard is a compound added to the concentrated combined extract of all sample components just before an aliquot of the extract is injected onto the chromatographic column. The internal standards are distinguishable from unknowns in the source stream by the fact that they are all deuterated analogs of compounds that may be encountered.

There are still two other deuterated compounds in the extract analyzed, which are not listed in Table 41, that are referred to as spikes. These compounds are 2,4-dichlorophenol-d_3 and 1,2,4-trichlorobenzene-d_3. They are not listed in Table 41 because data relevant to these compounds are obtained separately. The spike compounds are added to the XAD resin used in the sampling train before the sampling operation is performed; they are employed to determine whether they and similar compounds actually sampled are able to survive the sampling environment.

Compounds that were evident in the sample analysis but not identified as target compounds were subjected to identification by the procedure already described with volatile organics. That is, if the mass spectrum of an unidentified compound could be matched against the mass spectrum of a compound in the spectral library, identification would be established.

5.4.5.2 Illustrative Chromatogram. Selected chromatograms will be used subsequently in the discussion of the experimental results on unidentified compounds. As a background for the chromatograms presented later, a relatively simple chromatogram will be shown, to illustrate the peaks due to surrogates and internal standards. This illustrative chromatogram is for a field blank, which contains none of the peaks for substances encountered only in the field samples. (A field blank is an XAD cartridge that was transported to the field, opened to the ambient field laboratory atmosphere, sealed, and then treated in the laboratory as though it were part of an actual sample.)

Figure 10 shows the chromatogram for a field blank from the baseline test series. Peaks numbered 2, 19, 38, 57, and 68 are for the surrogates (the peak that corresponds to Surrogate 1 is not labeled); the peaks numbered 9, 29, 45, 62, 72, and 79 are for the internal standards (identities of these compounds may be seen in Table 41). The surrogates would have been present at concentrations of 10-20 μg/mL in the extract analyzed if they had been completely recovered; they were actually recovered at levels of about 25-50%. The internal standards were all present in the extract at the added concentration of 40 μg/mL.

5.4.5.3 Target Compounds - Identities and Concentrations. The compounds from the target list in Table 41 that were identified in the samples from the flue gas ducts in the baseline and low-NO_x tests are listed in Table 42. As is obvious from a glance at the table, the list of identified compounds is not long; moreover, as will be shown subsequently, the list of compounds that were identified is short in comparison with the number of compounds that were detected in the chromatographic analysis but not identified.

Some of the compounds in Table 42 appear to be actual components of the flue gas stream, whereas others are likely to be contaminants introduced by imperfect experimental procedures. Phenol was present in every sample, and benzoic acid was present in most of the samples. These two compounds are regarded as probable components of the gas streams. 2-Nitrophenol is similarly regarded, although it appeared but once. Naphthalene and 2-methylnaphthalene are also likely to have been present in the flue gas ducts. The two phthalate esters, on the other hand, are presumed to be contaminants introduced from sampling practices in the field or from analytical steps in the laboratory.

Only one of the target PAH compounds in Table 40 (naphthalene) was identified, and this occurred for only one inlet sample in the low-NO_x series. A derivative of naphthalene (2-methylnaphthalene) was also identified in the same sample. It is fairly clear that neither naphthalene nor any other of the 16 PAHs in Table 40 occurred with any frequency in the samples from the low-NO_x series at flue gas concentrations above the detection limit of about

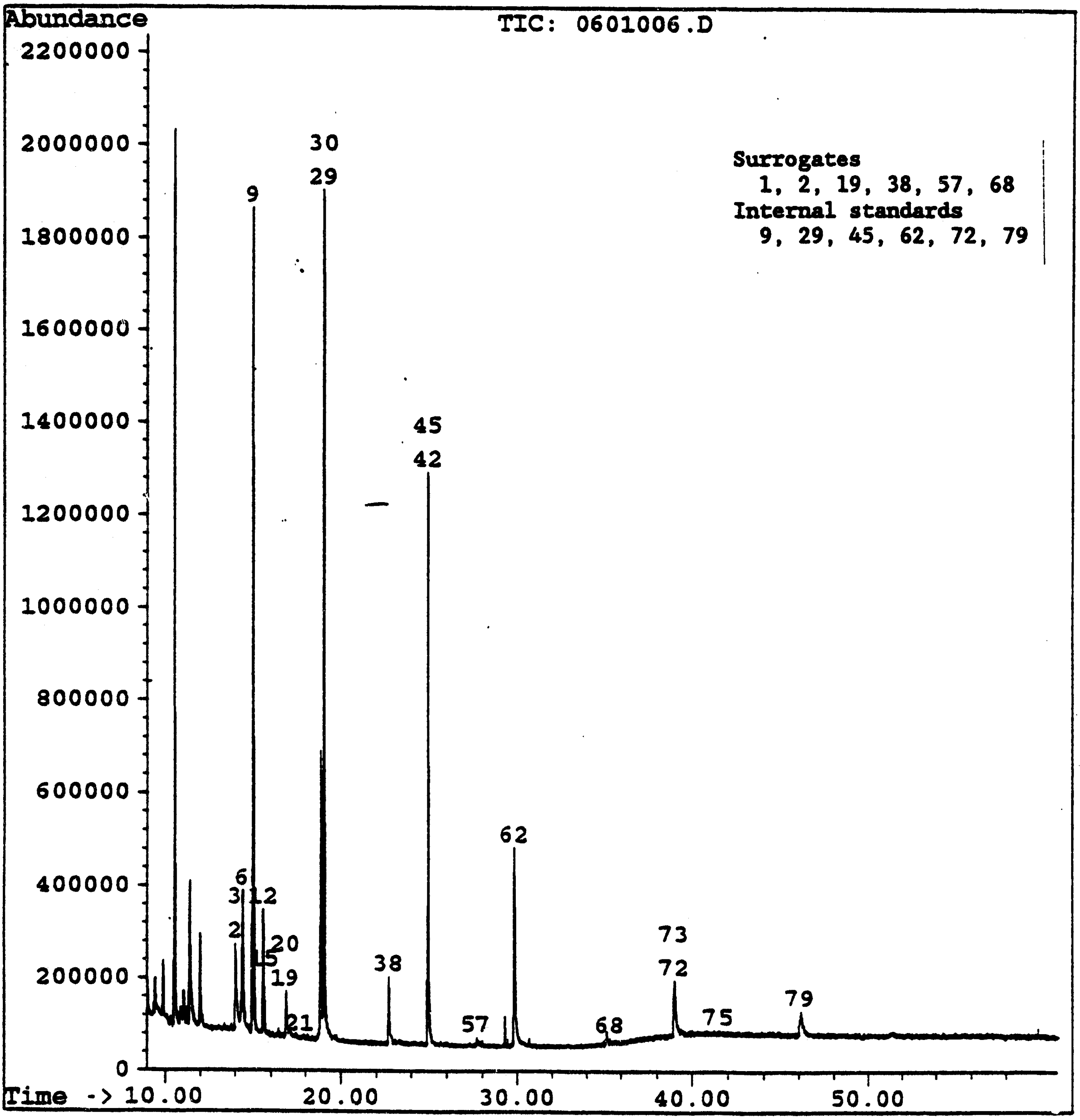


Figure 10. Ion chromatogram of field blank for semi-volatiles showing peaks for surrogates and internal standards.

2 $\mu g/Nm^3$. On the other hand, these compounds cannot be ruled out with the same degree of certainty in the baseline series because the detection limit was higher as the result of a larger final extract volume. The detection limit for the baseline series was approximately 20 $\mu g/Nm^3$.

The main questions of interest have to do with the influence of the two ESPs on changes in the concentrations of semi-volatiles across the ESPs and the influence of the change in combustion conditions on the occurrence of semi-volatiles. These issues are taken up in the paragraphs that follow.

It may seem unreasonable even to consider the influence of the ESPs on the compounds listed in Table 42, because the precipitation process is not likely to influence the concentrations of compounds that occur in the vapor state. The volatilities of phenol and benzoic acid, although less than the volatilities of benzene and toluene, are nevertheless high enough for both compounds at the concentrations reported to occur entirely in the vapor state in the range of temperatures where the ESPs operate. On the other hand, although potentially occurring in the vapor state, the compounds may be adsorbed on fly ash particles and thereby be subjected to removal in the ESPs.

With respect to the influence of the ESPs, there is first the question of the cold-side ESP. With only one experiment in each test series having been performed with the cold-side ESP energized, it is difficult to be certain of any conclusion. Moreover, the data set is incomplete in that no inlet sample was collected on the first occasion when the cold-side ESP was energized. (The absence of this sample is due to the fact that a successful leak check of the sampling train could not be completed even at a late evening hour; finally, the sampling run had to be cancelled. This action seemed justifiable since the composition of the gas stream at the inlet of the ESP system could not have been affected by the energization of the cold-side unit and inlet samples to be taken later should have been representative on the occasion when the sample was missed.) About all that can be said about the cold-side ESP is that it gave no evidence of an effect on semi-volatiles that was not also apparent as the effect of the hot-side ESP alone.

When the hot-side ESP alone was energized, the compounds believed to have been present as actual components of the flue gas stream were found at lower concentrations at the outlet than at the inlet, with one exception. That exception occurred with benzoic acid in the experiment on September 21. Superficially, therefore, there is evidence that the hot-side ESP removed significant amounts of the semi-volatile organics, and there is the presumption that the removal must have occurred because the organics were physically bound up with the fly ash being precipitated.

The concluding statement in the preceding paragraph, it will be seen, can only be allowed to stand if it is supported by the occurrence of organic matter on the fly ash removed from the hoppers of the hot-side ESPs. Unfortunately, the experiments to determine organic matter in the hopper ash did not identify any organic compound attributable to the flue gas environment. (As previously stated in Section 5.3, only phthalate esters were found, and these compounds were believed to be due to contamination of the ash samples in the laboratory. The concentration of benzoic acid in the hopper ash should have been of the order of 10 μg/g, provided that it had occurred in the same ratio to the ash in the hopper as to the ash in the flue gas entering the hopper. At this level, benzoic acid should have been seen, since the nominal limit for the detection of benzoic acid in a solid is 0.75 μg/g.)

Thus, the fate of the target compounds found relatively frequently in the samples from the gas stream is not known. One possibility, however, is removal from the system by oxidation, with ozone in the ESP corona regions being a possible oxidizing agent.

5.4.5.4 Unidentified Compounds. Figures 11 and 12 are the chromatograms for inlet and outlet samples for September 19, 1991, during the baseline test series, while the cold-side ESP was not energized. Both of these chromatograms, it must be noted, have ion currents on the vertical axis that range up to 10 times as high as the ion currents in the preceding chromatogram. These two chromatograms are thus not visually comparable to the previous one, but they are comparable with each other.

The most striking difference between the two chromatograms is that the inlet chromatogram is far more cluttered with peaks in the range of retention times from 10 to 30 min than is the outlet chromatogram. Another striking feature of the inlet chromatogram is that the peaks that are so visually dominant are far larger than those of the two target compounds that

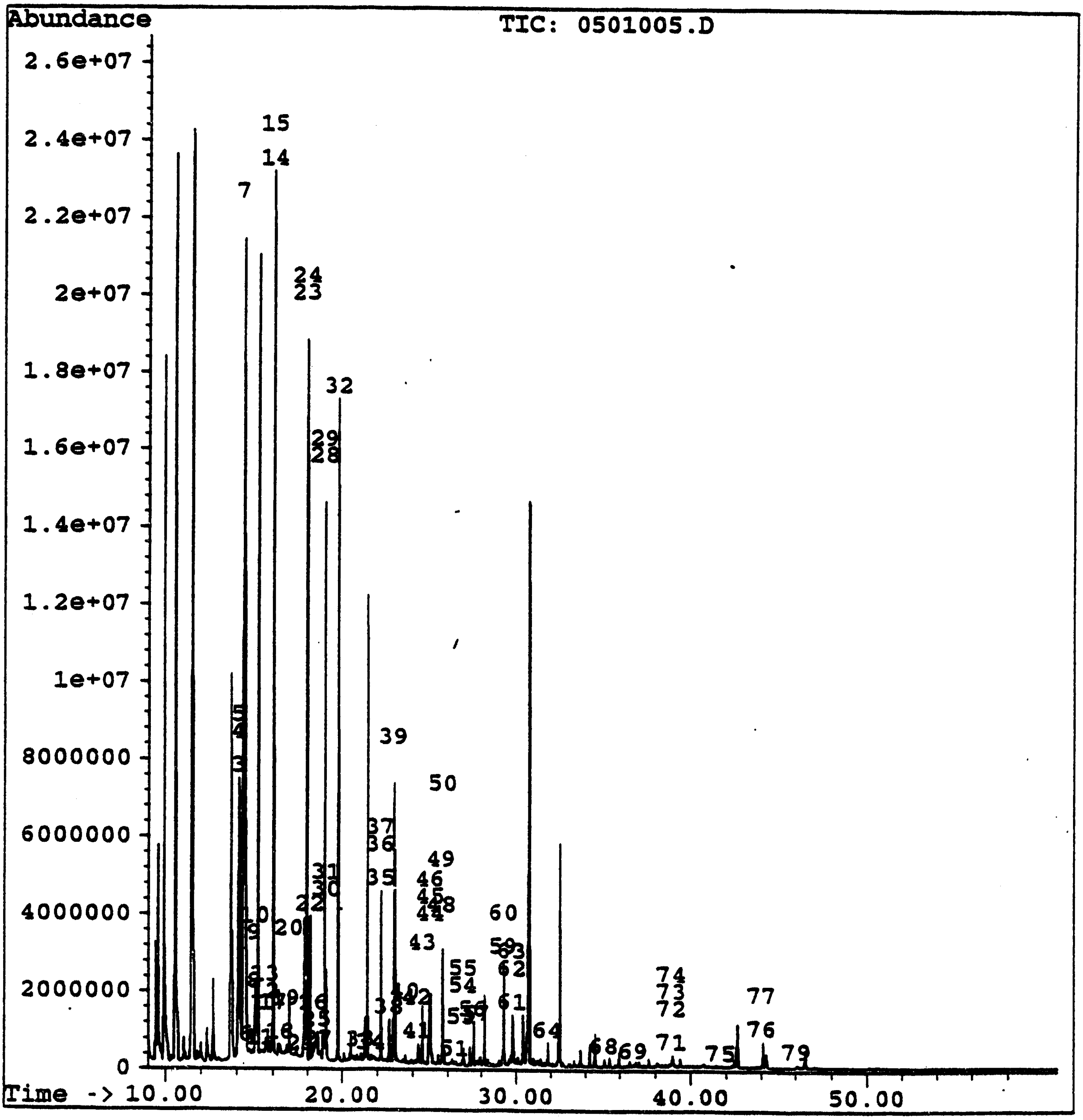


Figure 11. Ion chromatogram of semi-volatiles from ESP inlet in baseline testing.

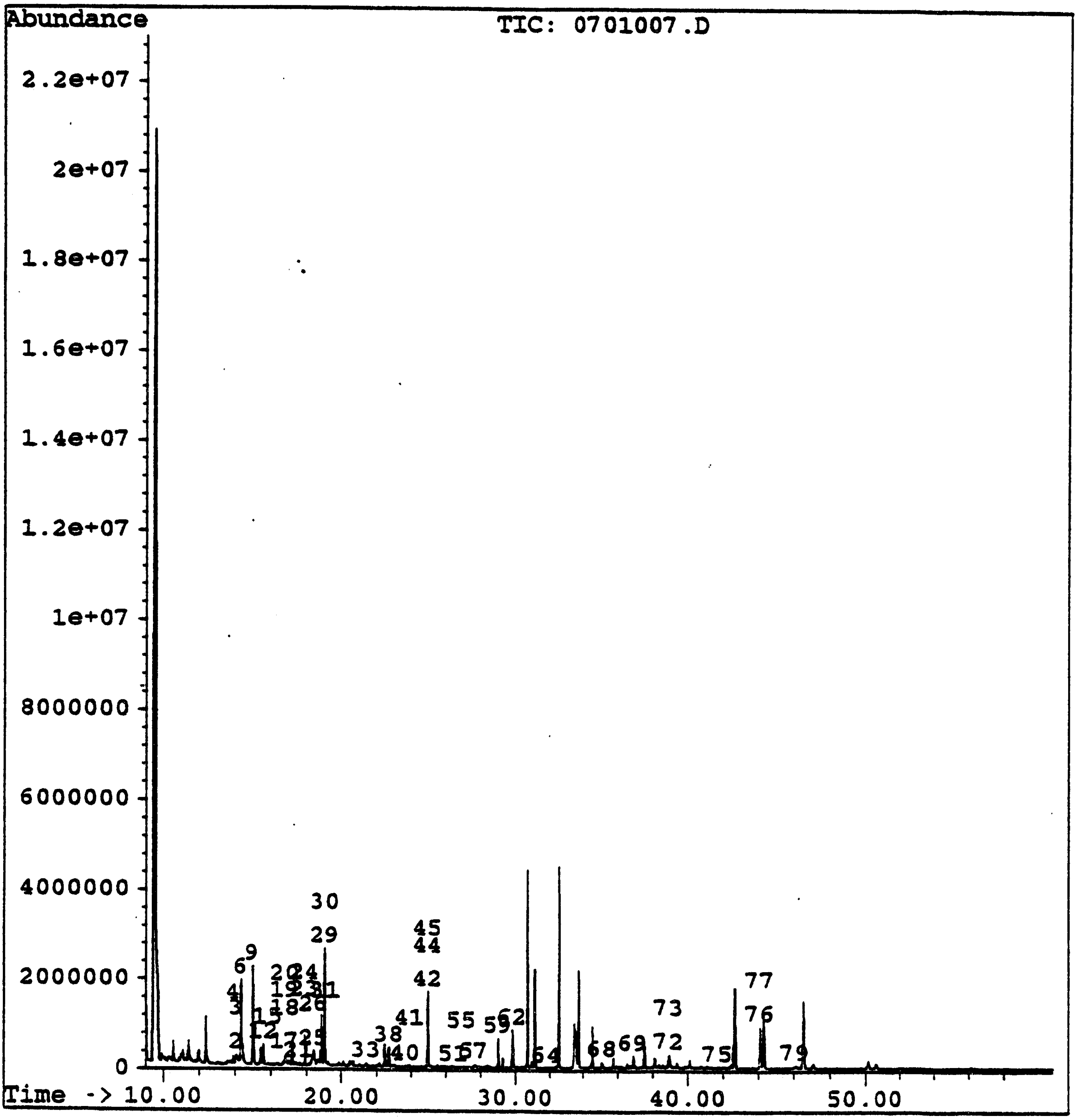


Figure 12. Ion chromatogram of semi-volatiles from ESP outlet in baseline testing.

were identified, phenol and benzoic acid, which are Compounds 3 and 25, respectively. Neither of these peaks is labeled, but they correspond to analyte concentrations of 56.6 and 18.1 μg/mL, whereas the 10 largest unidentified peaks for the range in retention times from 10 to 30 min range in concentration from 30 to 230 μg/mL.

Eight of the ten most prominent unidentified peaks for the inlet sample portrayed in Figure 11 were tentatively identified as silicone compounds. They were thus identified by the computer matching of the ion mass spectra of the unknowns against mass spectra of compounds in the reference library. On the other hand, only one of the seven compounds prominent enough in the outlet chromatogram for identification to be attempted was tentatively identified as a silicone compound.

Silicones are compounds frequently encountered as contaminants in work of the type described here. Thus, consideration must be given to two possibilities: 1) silicones were introduced somehow as contaminants in the inlet sample but not the outlet sample, or 2) silicones actually occurred in a prominent way in the flue gas at the ESP inlet but not in the flue gas at the ESP outlet (reflecting, by inference, the removal of silicones in the hot-side ESP). It seems most likely that silicone contamination occurred selectively in the inlet sample and that it perhaps occurred during the sampling event, not the subsequent laboratory analysis.

Silicone lubricant obviously has to be considered as the source of the silicone compounds detected, but no such lubricant was deliberately used. (For effecting seals at ball-and-socket joints in the sampling train, silicone grease was avoided, but a fluorinated polymer from Dupont, Krytox, was used.) The most likely source of the silicone compounds detected is believed to be some inner component of the probe, perhaps a glass-fiber lubricant associated with the glass-fiber sleeve that held the electrical heating wire around the Pyrex liner. The inlet duct was under a significantly negative pressure; ambient air could have swept through the probe into the duct (passing between the metal sheath and the jacketed, heated liner), thus sweeping out silicone vapors that may have been evolved at the 700 °F sampling temperature. Such silicone vapors would have entered the duct near the sampling nozzle and could thus have become part of the sample being collected.

Even though the silicone compounds seemed to disappear between the inlet and outlet of the ESPs, they were not found in the ESP ash, just as the target compounds phenol and benzoic acid were not found.

Figures 13 and 14 are comparable to the two figures discussed above except that they are from the low-NO_x test series rather than the baseline series. They are samples collected at the inlet and outlet of the ESPs on January 15, 1992, when the cold-side ESP was not energized. The visual contrast between inlet and outlet chromatograms here for low-NO_x conditions is less striking than the contrast for the inlet and outlet chromatograms discussed for baseline conditions. Indeed, the estimated concentrations of the unidentified compounds in the low-NO_x samples show that for the retention time range of 10-40 min the total concentration of these compounds in the extract is somewhat greater at the outlet than at the inlet — 433 μg/mL versus 404 μg/mL.

Only one of the unidentified compounds at the inlet is a silicone compound and none at the outlet is a silicone compound. Thus, the cause of contamination that existed during the baseline test series apparently did not exist during the low-NO_x test series. Moreover, and more to the point insofar as the purposes of this study were concerned, low-NO_x conditions in the boiler evidently produced a substantially elevated total concentration of semi- volatile compounds, which unfortunately could not be identified satisfactorily.

Table 43 lists the most ten most concentrated unknowns from the inlet and outlet data discussed above. The compounds are listed in the order of increasing retention times. The other data given are the estimated concentrations in the extract being analyzed and the numerical rating to designate the quality of the tentative identification (the term is Qual; the values range from 0 at the bottom to 100 at the top). Where there are multiple possibilities for compound identification, the one with the highest Qual value is listed in Table 43, unless some compound with a lower Qual value in one sample matches a compound with a similar retention time in the other sample. Thus, guanidine with a retention time of about 9.9 min is listed for both samples; it has the second ranking Qual value for the inlet sample but the top ranking for the outlet.

If near agreement in retention times and agreement in tentative identifications between inlet and outlet unknowns are essential criteria, the conclusion is that only two of the compounds

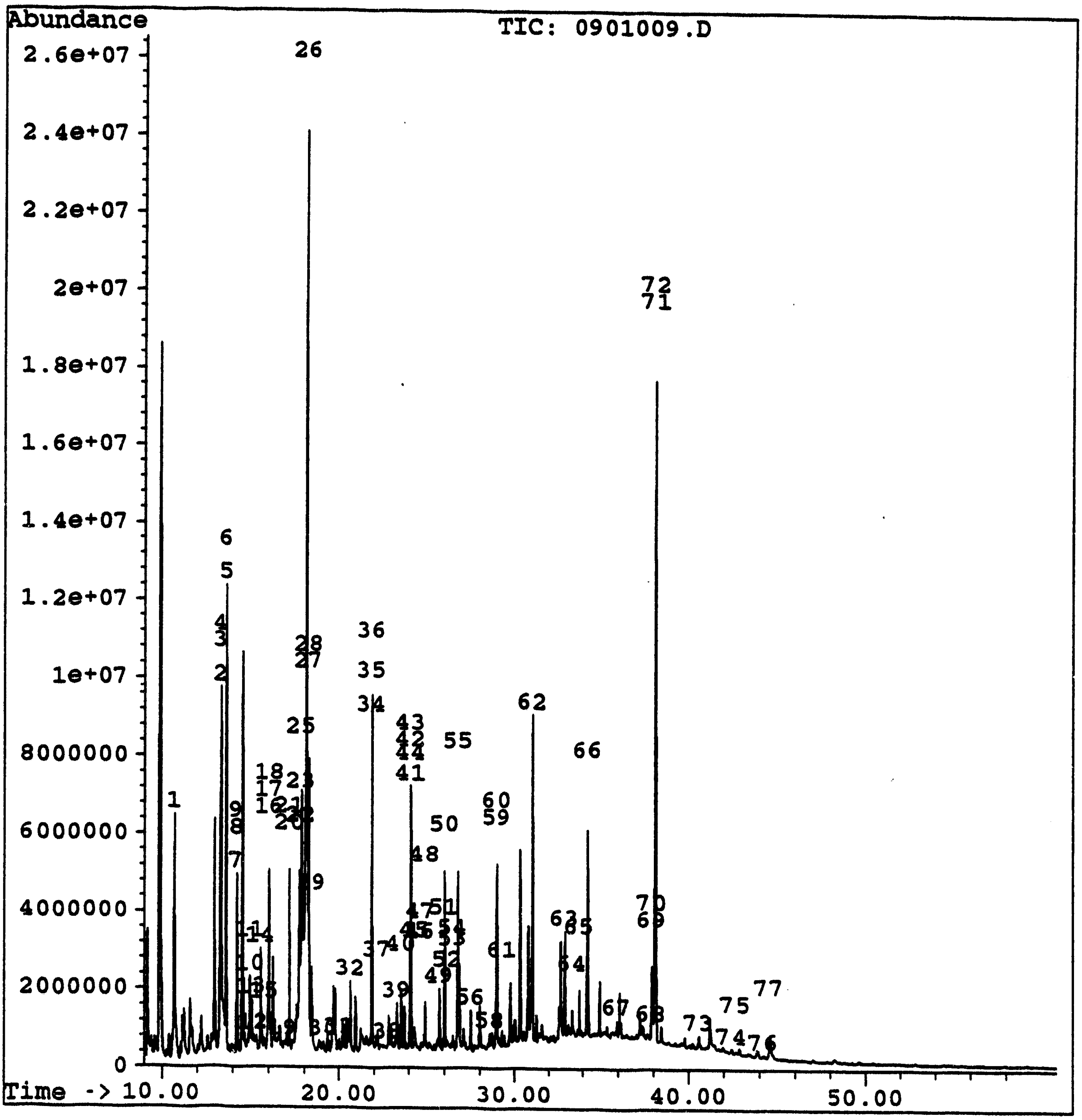


Figure 13. Ion chromatogram of semi-volatiles from ESP inlet in low-NO_x testing.

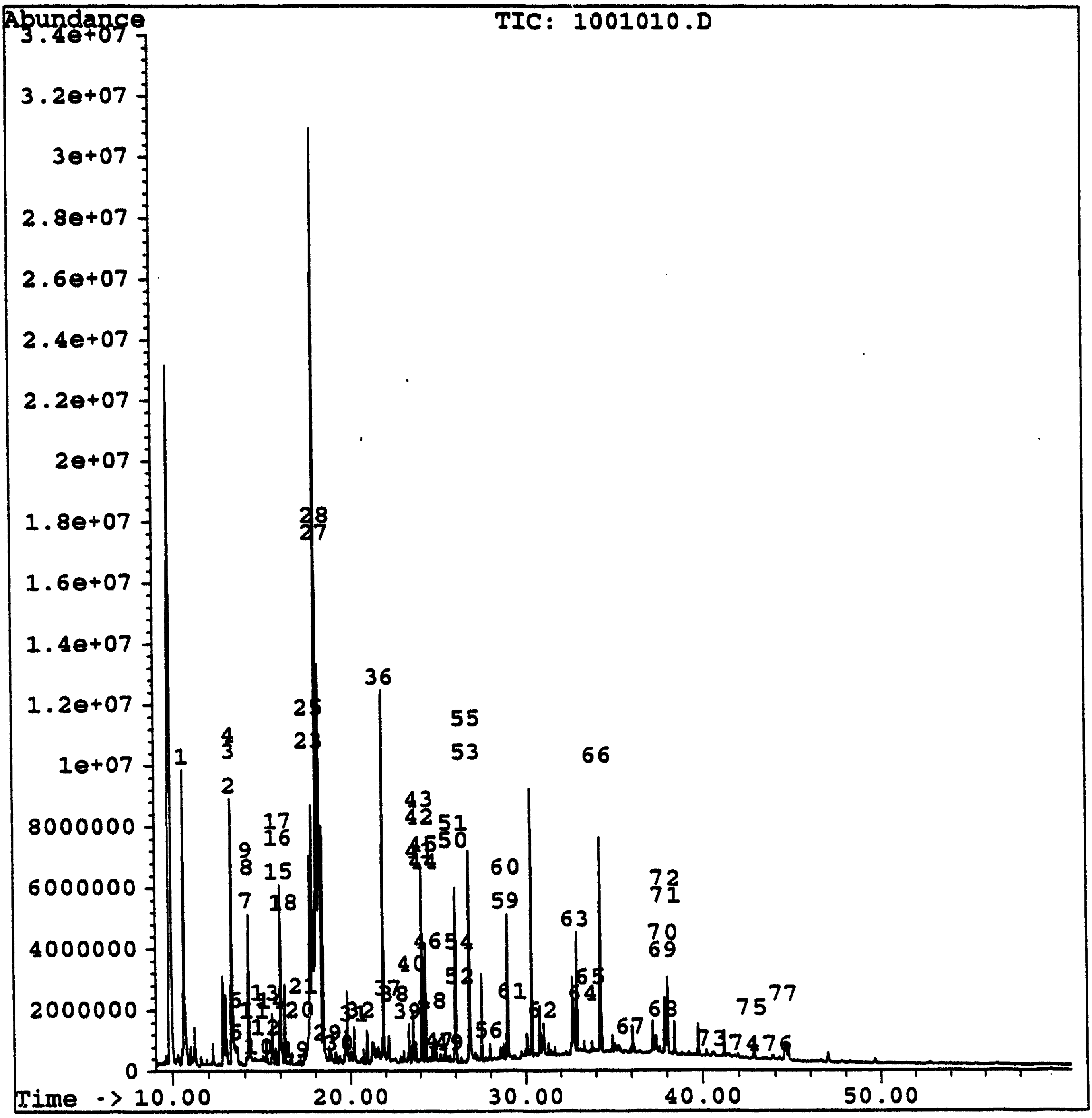


Figure 14. Ion chromatogram of semi-volatiles from ESP outlet in low-NO_x testing.

listed are common to both inlet and outlet samples. The number of compounds that can be assumed common to both samples increases if unknowns in addition to the ten at the highest concentrations are considered. Even so, there is no way to avoid the impression that the unknowns at the inlet and the outlet are, in the main, different compounds.

The questions that follow from the foregoing conclusion — what happens to the inlet compounds that are not found at the outlet, and where do the outlet compounds come from if they are not present at the inlet — must be given answers that are only speculative. One conceivable answer — that the inlet compounds were found in the ESP hopper ash — is refuted by the analytical results for the ash. Another answer that cannot be either confirmed or refuted is that the residence time within the system possibly led to chemical changes. A compound might disappear altogether as a consequence of oxidation, or it might be chemically altered as the result of partial oxidation or some type of reaction. As stated previously, ozone in the corona regions of the ESP is a possible reactant that leads to destruction or alteration. Even if the rate of chemical alteration were slow, the compound might disappear from the gas stream during the transit time from the hot-side ESP inlet to the cold-side ESP outlet (probably a time of the order of 10 sec) as the result of its removal with precipitated ash and then reach the final altered chemical state during the longer time that the compound resides with the ash in the 700 °F zone of the hot-side ESP.

Table 40
Semi-Volatile Target Compounds of the PAH Type

Acenaphthylene	Chrysene
Acenaphthene	Dibenzo(a,h)anthracene
Anthracene	Fluoranthene
Benzo(a)anthracene	Fluorene
Benzo(a)pyrene	Indeno(1,2,3-cd)pyrene
Benzo(b)fluoranthene	Naphthalene
Benzo(g,h,i)perylene	Phenanthrene
Benzo(k)fluoranthene	Pyrene

Table 41
Target Semi-Volatile Compounds of Extended Types[a,b]

No.	Compound	Detection limit, $\mu g/Nm^3$
1	2-Fluorophenol SURR1	-
2	Phenol-d_5 SURR2	-
✓3	Phenol	5
✓4	Aniline	5
✓5	Bis(2-Chloroethyl) ether	3
7	2-Chlorophenol	5
8	1,3-Dichlorobenzene	5
9	1,4-Dichlorobenzene-d_4 IS1	-
✓10	1,4-Dichlorobenzene	5
11	Benzyl alcohol	5
✓13	1,2-Dichlorobenzene	5
14	2-Methylphenol	5
15	Bis(2-Chloroisopropyl) ether	3
16	4-Methylphenol	5
17	N-Nitroso-di-N-propylamine	5
✓18	Hexachloroethane	3
19	Nitrobenzene-d_5 SURR5	-
✓20	Nitrobenzene	5
✓21	Isophorone	5
23	2,4-Dimethylphenol	3
24	2-Nitrophenol	5
25	Benzoic acid	5
26	Bis(2-Chloroethoxy) methane	3
27	2,4-Dichlorophenol	8

Table 41 (Continued)
Target Semi-Volatile Compounds of Extended Types[a,b]

No.	Compound	Detection limit, µg/Nm^3
✓28	1,2,4-Trichlorobenzene	6
29	Naphthalene-d_8 IS2	-
✓30	Naphthalene	3
31	4-Chloroaniline	5
✓32	Hexachlorobutadiene	3
33	4-Chloro-3-methylphenol	5
34	2-Methylnaphthalene	3
35	2,4,6-Trichlorophenol	5
✓36	Hexachlorocyclopentadiene	5
37	2,4,5-Trichlorophenol	8
38	2-Fluorobiphenyl SURR6	-
39	2-Chloronaphthalene	3
40	3-Nitroaniline	3
✓41	Dimethyl phthalate	3
42	2.6-Dinitrotoluene	3
43	Acenaphthylene	5
44	2-Nitroaniline	3
45	Acenaphthene-d_{10} IS3	3
46	Acenaphthene	-
✓47	2,4-Dinitrophenol	5
✓48	4-Nitrophenol	8
✓49	Dibenzofuran	5
✓50	2,4-Dinitrotoluene	3
51	Diethyl phthalate	3

Table 41 (Continued)
Target Semi-Volatile Compounds of Extended Types[a,b]

No.	Compound	Detection limit, $\mu g/Nm^3$
52	4-Chlorophenyl phenyl ether	3
53	Fluorene	3
54	4-Nitroaniline	5
55	4,6-Dinitro-2-methylphenol	5
56	N-Nitrosodiphenylamine	8
57	2,4,6-Tribromophenol SURR7	-
58	4-Bromophenyl phenyl ether	3
✓59	Hexachlorobenzene	8
✓60	Pentachlorophenol	8
61	Phenanthrene	3
62	Phenanthrene-d_{10} IS4	-
63	Anthracene	3
64	Di-n-Butyl phthalate	3
65	Fluoranthene	5
✓66	Benzidine	3
67	Pyrene	30
68	Terphenyl-d_{14} SURR8	-
69	Butyl benzyl phthalate	5
✓70	3,3'-Dichlorobenzidine	8
71	Benzo (a) anthracene	3
72	Chrysene-d_{12} IS5	-
73	Bis(2-Ethylhexyl) phthalate	5
74	Chrysene	5
75	Di-N-Octyl phthalate	5

Table 41 (Concluded)
Target Semi-Volatile Compounds of Extended Types[a,b]

No.	Compound	Detection limit, $\mu g/Nm^3$
76	Benzo (b) fluoranthene	5
77	Benzo (k) fluoranthene	5
78	Benzo (a) pyrene	5
79	Perylene-d_{12} IS6	-
80	Indeno (1,2,3-cd) pyrene	8
81	Dibenz (a,h) anthracene	8
82	Benzo (g,h,i) perylene	8

[a] Surrogates and internal standards are designated distinctly. SURR3 and SURR4 were not used in this work. Compounds listed in Title III of the 1990 Clean Air Act Amendments are designated by check marks. Compound numbers 6, 12, and 22 were not assigned.

[b] The detection limits given here are based on assumptions of a gas volume of 2 Nm^3 (lower than any actual volume in this work) and an extract volume of 1 mL. The latter was achieved in the low-NO_x work but not in the baseline work. The 10-mL extract volume in the latter case multiplied the detection limit by 10.

Table 42
Semi-Volatile Compounds Identified in Baseline and Low-NO_x Tests

Test series	Test date	Cold-side ESP mode	Compound	Concn, $\mu g/Nm^3$	
				Inlet	Outlet
Baseline	9/18/91	On	Phenol	–	86
			Benzoic acid	–	50
	9/19/91	Off	Phenol	566	<33
			Benzoic acid	181	69
	9/20/91	Off	Phenol	453	40
			Benzoic acid	172	93
	9/21/91	Off	Phenol	53	<35
			Benzoic acid	62	124
Low NO_x	1/14/92	On	Phenol	82	20
			Bis(2-Chloroisoropyl ether)	13	<2
			2-Nitrophenol	<2	12
			Benzoic acid	267	<6
			Naphthalene	10	<2
			2-Methylnaphthalene	3.2	<2
			Diethyl phthalate	7.4	<2
			Di-N-butyl phthalate	35	<4
	1/15/92	Off	Phenol	30	3.6
			Diethyl phthalate	3.2	<2
			Di-N-butyl phthalate	21	<3
	1/16/92	Off	Phenol	68	71
			2-Nitrophenol	1.7	2.6
			Diethyl phthalate	6.2	<2
			Di-N-butyl phthalate	30	3.1
	1/17/92	Off	Phenol	52	3.7
			Benzoic acid	114	96
			Diethyl phthalate	5.0	<2
			Di-N-butyl phthalate	33	<3

Table 43
Comparison of Tentatively Identified Compounds for Inlet and Outlet Samples from the Low-NO_x Series

INLET

Retention time, min	Compound name	Concn. µg/ml	Qual.
9.89	Guanidine[a]	157.41	37
10.66	Phenol, 2-fluoro[b]	46.26	91
12.95	1-Propanone, 2-bromo-1-phenyl	36.23	47
13.30	Benzenesulfonic acid, 4-hydroxy	95.46	37
13.61	Cyclotetrasiloxane, octamethyl	55.11	91
14.50	Benzene, 1-methyl-3-(1-methylethyl)	51.95	94
16.02	Unknown	27.87	0
17.84	Benzothiazole, 2,2'-dithiobis	30.07	9
31.05	1,2-Benzenedicarboxylic acid, butyl	33.93	83
38.10	Bis(2-ethylhexyl) phthalate	30.15	91

OUTLET

Retention time, min	Compound name	Concn. µg/ml	Qual.
9.94	Guanidine[a]	290.32	37
10.68	Phenol, 2-fluoro[b]	67.76	91
13.27	Hexanoic acid, anhydride	79.47	42
16.02	Unknown	33.45	0
18.10	Pyridine, 2-chloro-3,4,5,6-tetrafluoro	44.72	38
21.88	1,1'-Biphenyl, 4-fluoro	53.07	96
26.00	Phenol, 2,4-bis(1-methylethyl)	31.27	46
30.35	Pentadecanoic acid, methyl ester	39.23	83
34.26	9H-Xanthen-9-one, 1,3,8-trihydroxy	30.51	40
42.86	Nonacosane	57.42	94

[a] The compounds are probably the same but probably are not guanidine: $(H_2N)_2C{=}NH$.

[b] The compounds may be the same but not the compound named. This compound was a surrogate and was detected as such at a retention time of about 10.6 min. The Qual value of 91, although high, does not make this a confirmed identification; the evidence disputes the tentative confirmation.

6. DATA ON MATERIAL BALANCE

6.1 TRACE ELEMENTS

6.1.1 General Considerations

The principles that must be used to learn whether the analytical data provide a material balance for an element in all relevant streams are considered in Table 44. The components of material balance considered here include the gas stream at the inlet of the hot-side ESP but nothing beyond that point. Arsenic is the element considered; the data cited are from the baseline test on September 18, 1991, when the cold-side ESP was operating. In the absence of flow rate data for some of the pertinent streams (a matter previously discussed in Section 2), hypothetical flow rates are stated. These hypothetical flow rates and the resulting fluxes of arsenic are shown in parentheses. They are adjusted as necessary to give an exact material balance whereas, based on the only hard data available, all that can be said is that 70% of the arsenic in the coal was recovered in the gas stream at the ESP inlet.

The hypothetical flow rates were given values on the basis of the following ideas:

- The flux of arsenic in the boiler seal water was set equal to zero. This water contributes arsenic to the gas stream leaving the boiler only if the arsenic component is vaporized. In the absence of any knowledge that arsenic could be vaporized from the water, the assumption that none occurs is the only logical assumption that can be made. (If the alternative assumption is made that the water contributed arsenic in an amount that is one-tenth of that provided by the coal, all of the arsenic in water supplied at the rate of 46,000 gal/min would have been vaporized. Surely, this would be an absurdity.)

- The rate of rejection of pyrite from the coal was estimated to be 2% of the feed rate of the coal. The specific concentration of arsenic in the pyrite, 6.4 μg/g, was assigned to make the overall material balance exactly even. It can be seen by reference to Table 10 that this concentration is within the range experienced, yet there is no way to assign a representative value because of the variability of the compositions of the pyrite samples analyzed.

- The rate of ash accumulation in the economizer hoppers is assumed to be 5% of the total ash. The concentration of arsenic in this ash is based on the actual analysis.

- The partitioning of coal ash between the bottom of the boiler and the fly ash entrained in the flue gas is assumed to be 20% as bottom ash and 80% as fly ash. The concentration of arsenic in the bottom ash is the observed value. If the water that had wet the ash before it was dried and analyzed made any contribution to the arsenic found, then, in principle, the fraction of the coal ash assumed to be in the bottom ash would be slightly less than 20%. (It could not be very different. The concentration of arsenic in the water was very small and not much water was associated with the bottom ash that was analyzed.)

For arsenic, the factor that seems likely to have the largest effect on material balance was the flow rate of the pyrite. This conclusion is due to the large uncertainty in both the rate at which pyrite is rejected and the average concentration at which arsenic appears in this material.

The term "recovery," referring to the percentage of an element in the coal that was found in the flue gas at the inlet of the hot-side ESP, has been selected to serve as an indirect measure for material balance. This has been done since the absence of some of the material flow rates prevents a rigorous test of material balance. Recovery obviously cannot, in principle, exceed 100%. It would be about 80%, assuming an 80/20 split between fly ash and bottom ash, for any element that is not discharged in the vapor state or discharged in the pyrite, bottom ash, or economizer, at a greatly enriched concentration. If an element were discharged primarily as a vapor, its recovery might reach 100%; if it were highly concentrated in the bottom ash, its recovery would be less that 80%.

If, then, a recovery of 80% is the norm for the trace elements as a group, what does a recovery of 70%, as in Table 44, mean for arsenic? It implies that arsenic is not discharged primarily as a vapor but that it may be somewhat enriched in the solids discharged before the flue gas reaches the ESP inlet. There are no data to support either of these hypotheses. Thus, the observed recovery is a plausible value, somewhat below the norm of 80% because of imperfect sampling and analysis.

6.1.2 Recoveries at the ESP Inlet

The data on element recoveries, based on fluxes expressed in g/min in the coal and the flue gas, are presented in five tables. Tables 45 and 46 present data based mainly on ICP analyses of samples from the Multiple Metals Train. Tables 47 and 48 give data based on neutron activation analysis of samples collected from the suspended state — in series cyclones in the baseline testing or in the metals train in the low-NO_x testing. Table 49 deals only with mercury determination in samples collected in the traps of soda lime and iodated carbon.

The following comments applying to Tables 45 and 46, based principally on ICP data, should clarify some of the "recoveries" for which exact numerical values are not given:

- The notation "??" denotes a flux in the gas stream that is consistent with the flux in the coal. However, because of insufficient analytical sensitivity, the latter can only be assigned a limiting value; thus, the recovery cannot be given a numerical value. This is often true for antimony, arsenic, and cobalt.

- The very high minimum values, such as >161, >256, and >239 that appear for lead in Table 45 are probably attributable to lead concentrations in the coal that are known only by upper limits. The true values presumably were above the limits cited for lead in the coal.

Certain additional comments applying to Tables 45 and 46 attempt to summarize information that is known (or believed correct) to account for divergences of the recoveries from the norm of 80%. These comments apply only to elements that have an average recovery in either table outside the recovery range 80 ± 20%, which reflects a reasonable range of experimental error. These additional comments are as follows:

- Arsenic. The data are unaccountably low in Table 46 for the low-NO_x testing. The problem is attributed to erroneous, low concentrations found in the samples from the gas stream. NAA yielded substantially higher values (see Table 48).

- Barium. The high recoveries in Table 46 may be due to incomplete dissolution of the ash in the coal and thus due to faulty values of the concentration in the coal. Still, there was clearly a problem with the analyses of the samples from the flue gas, which required two steps of digestion. Most of the barium reported was obtained in the second digestion.

- Cadmium. The variation of concentrations in the flue gas appeared to be too great to be plausible. Errors in the concentration in the gas phase are the likely explanation for the wide range of recoveries.

- Chromium. The high recoveries are probably due to low values for the element in the coal.

- Copper. The recoveries of copper averaged about 70% in the baseline testing but only about 28% in the low-NO_x testing. Superficially, the explanation appears to lie in differences in copper concentrations in the coal, which appeared to be higher in the second test series.

- Mercury. The recoveries have an average around 25% and thus are not in agreement with the idea that a volatile metal might have a recovery above the norm. The problem lies with a known deficiency in the analysis of peroxide impingers from the metals train, where mercury was not recovered properly. The data for mercury in Table 49 must be considered in place of that in Tables 45 and 46.

- Phosphorus. Recoveries of phosphorus appeared low only in the data for the low-NO_x testing. Yet, ICP must be regarded as unusually undependable for measuring phosphorus. The concentrations of this element in the coal based on ICP data were

30% or less of the concentrations derived from data based on colorimetric determination of phosphate in coal ash.

- Selenium. In some instances, this volatile element was recovered at levels above the norm of 80%, as expected for volatile elements. The data for the low-NO_x testing, however, generally departed from this behavior. Selenium was an element that gave persistent analytical problems.

The recovery data in Tables 47 and 48, based on neutron activation analysis, are generally nearer the norm than those already discussed, which were based on ICP. Even so, the NAA data are based only on solids. They contain no contributions from substances that were in the vapor state and thus subject to collection in impingers.

Although apparently superior to the ICP data for element recovery, the NAA data still present problems. For some elements — mercury and nickel, for example — there are undefined recoveries. For others, such as chromium, the data are more credible than the results from ICP. The data for arsenic and selenium require particular attention. Arsenic, for example, had an average recovery of 53% in the baseline testing and an average of 139% in the low-NO_x testing. Selenium had an average of 6% in the former and 98% in the latter. The fact that there was a difference in the sources of the solids analyzed has to be brought up in connection with the anomalies for arsenic and selenium. In the baseline testing, the solids were composites of ash collected from the duct, at 700 °F, with the series cyclones. In the low-NO_x testing, the solids were from the front half of the metals train and were thus collected at temperatures that decreased to 250 °F at the filter. The volatile element, selenium, was thus brought out of the vapor state, incorporated in the sample analyzed, and more fully recovered in the low-NO_x testing. The other element, arsenic, might be said to appear volatile also on the basis of the differences in recovery in the two kinds of solids, but there are compelling data from other sources to believe that arsenic was not largely present as vapor. The disparity in data for arsenic cannot be explained.

Table 49 tells a refreshing story of relatively high success with mercury from the sampling train with solid sorbents. The data on this element, clearly volatile, are from the ESP outlet. In the baseline testing, the average recovery of mercury was 0.092/0.082 x 100 = 112%. In the low-NO_x testing, the recovery was 80%.

6.1.3 Balance in the ESP System

Tables 50 and 51 give an analysis of material balance in the ESP system. Two factors are compared: 1) the rate at which each element was removed from the gas stream and 2) the rate at which the element was collected in the ESP hoppers. The first of these factors was calculated as the difference between inlet and outlet values of the product of gas flow rate and element concentration. The second factor was calculated as the product of element concentration in the hopper solids and the total solids accumulation rate. The accumulation rate of total solids was calculated as the difference between inlet and outlet values of the product of gas flow rate and total solids concentration. The ratio of the accumulation rate in the ESP to the loss rate from the flue gas, as a percentage, is termed "closure."

Indefinite results were obtained for mercury in both test series and for antimony, beryllium, and selenium in the second. There are some poor or even absurd results, mainly in the second test series, as illustrated by closure figures of 200% for barium and 211% for cadmium. Generally speaking, however, the data are satisfactory. They show conclusively that arsenic was removed from the gas stream as a component of the solids in the ESP and that mercury and selenium, on the other hand, were retained in the vapor state at the ESP outlet.

6.2 HALOGENS AND SULFUR

Numerical values of the recoveries of coal sulfur as SO_2 and coal halogens as HF and HCl have already been given in Section 5.4.2. The following is a summary of data from the two sampling trains (controlled condensation train and Acid Gases Train):

		Element recovery, %	
Element	**Sampling**	**Baseline testing**	**Low-NO_x testing**
Sulfur	CCT, inlet	90 ± 3	84 ± 1
	CCT, outlet	94 ± 8	87 ± 10
	AGT, inlet	96 ± 46	81 ± 21
	AGT, outlet	107 ± 19	85 ± 18
Fluorine	AGT, inlet	49 ± 29	80 ± 14
	AGT, outlet	79 ± 19	82 ± 9
Chlorine	AGT, inlet	80 ± 31	82 ± 9
	AGT, outlet	98 ± 25	120 ± 6

The recoveries are considered satisfactory. A portion of the sulfur not included here was discharged in the pyrite, and part was incorporated in the fly ash. Portions of the halogens may have been incorporated in the ash as fluoride and chloride salts, but long experience with analyzing water extracts of fly ash by ion chromatography suggests that not much of the halogens was combined with the ash. Analysis of extracts of selected samples of solids from the front half of the Acid Gases Train confirmed that negligible fractions of the halogens were combined with the ash.

6.3 ORGANIC COMPOUNDS

No attempt was made to construct material balance for organic compounds. There was no effort made to determine the concentrations of these compounds in the coal, although their presence was to be expected. Garcia et al. (12) have reported the concentrations of individual organic compounds in a number of coals. The combustion process, however, is certain to destroy part of the original organic content of the coal and is likely also to create new organic compounds from more complex compounds. Material balance for an organic compound, therefore, would be coincidental if it existed.

Table 44
Illustration of Material Balance
(arsenic in baseline test of September 18, 1992)

Stream	Flow rate[a]		Concn of As		Element flux[a]
Input					
Coal	166,180 lb/hr	x	1.65 μg/g	=	2.10 g/min[b]
Boiler seal water	[0 gal/min]	x	0.0012 μg/mL	=	0 g/min
Output					
Pyrite	[3324 lb/hr]	x	6.4 μg/g	=	[0.16 g/min]
Bottom ash	[2988 lb/hr]	x	3.54 μg/g	=	[0.08 g/min]
Economizer ash	[747 lb/hr]	x	71.5 μg/g	=	[0.40 g/min]
Gas stream	10,914 Nm^3/min	x	134 μg/Nm^3	=	1.46 g/min[b]
			Total	=	2.10 g/min

[a] Rates in parentheses are hypothetical, as described in the text. Pyrite, 2% of coal; bottom ash, 20% of coal ash; economizer ash, 5% of coal ash.
[b] Actual recovery = 100 x 1.46/ 2.10 = 70%.

Table 45
Recovery of Coal Trace Elements in Flue Gas at the ESP Inlet – Baseline Testing, ICP/AAS Analysis, September 1991

	9/18/91			9/19/91			9/20/91			9/21/91		
	Flux, g/min		Recovery, %	Flux, g/min		Recovery, %	Flux, g/min		Recovery, %	Flux, g/min		Recovery, %
	Coal	Gas		Coal	Gas		Coal	Gas		Coal	Gas	
As	2.10	1.47	70	2.59	2.10	81	1.98	2.37	120	3.01	2.66	88
Ba	35.8	11.8	33	30.5	25.8	85	29.0	25.4	88	42.6	29.5	69
Be	<0.6	0.723	>120	0.76	0.41	54	0.72	0.739	103	1.07	0.784	73
Cd	2.73	9.44	346	2.23	14.4	646	2.00	1.52	76	1.44	1.56	108
Co	1.26	1.50	119	2.67	2.30	86	2.85	1.81	64	1.35	1.95	145
Cr	5.14	9.03	176	6.6	11.4	173	9.46	12.1	128	6.73	12.4	184
Cu	6.81	4.80	70	7.96	3.72	47	7.57	6.14	81	6.98	5.57	80
Hg	0.078	0.019	24	0.088	0.021	24	0.087	0.012	14	0.076	0.054	71
Mn	24.9	4.95	20	23.2	21.0	91	18.5	18.8	101	19.0	23.0	121
Mo	6.05	6.83	113	6.54	8.27	127	5.82	5.67	97	4.32	7.72	179
Ni	8.4	6.02	72	9.5	8.14	86	9.7	8.57	88	6.62	8.24	124
P	24.4	13.6	56	15.8	14.2	90	13.7	10.4	76	12.77	14.4	113
Pb	<6	9.65	>161	10.4	13.6	131	<6	15.4	>256	<6	14.3	>239
Sb	<3	1.09	??	<3	1.76	??	<3	1.43	??	<3	1.32	??
Se	0.69	0.253	37	0.76	0.464	61	0.73	0.429	59	0.72	0.525	73
V	43.1	43.0	100	61.3	45.5	74	48.1	35.6	74	86.1	47.2	55

Table 46
Recovery of Trace Elements in Flue Gas at the ESP Inlet – Low-NO$_x$ Testing, ICP/AAS Analysis, January 1992

	1/14/92			1/15/92			1/16/92			1/17/92		
	Flux, g/min		Recovery, %	Flux, g/min		Recovery, %	Flux, g/min		Recovery, %	Flux, g/min		Recovery, %
	Coal	Gas		Coal	Gas		Coal	Gas		Coal	Gas	
As	3.10	0.90	29	<2.5	1.18	??	<2.5	0.69	??	3.53	1.19	34
Ba	48.3	78.7	163	46.9	78.8	168	40.2	87.3	217	41.2	73.6	179
Be	0.81	0.72	89	0.71	0.80	113	2.42	0.54	22	2.54	0.71	28
Cd	2.44	0.78	32	2.69	4.46	166	2.62	0.68	26	2.53	1.60	63
Co	<2.5	2.27	??	<2.5	2.11	??	<2.5	1.87	??	<2.5	2.05	??
Cr	11.1	16.1	145	10.1	8.43	83	11.8	7.92	67	11.7	13.1	112
Cu	22.7	5.90	26	17.1	3.84	22	18.0	4.50	25	18.6	6.84	37
Hg	0.167	0.039	24	0.084	0.020	24	0.033	0.015	44	0.094	0.013	14
Mn	21.5	16.8	78	18.8	12.1	64	19.5	17.6	90	21.2	14.3	67
Mo	12.5	10.9	87	8.68	8.25	95	11.0	9.26	84	12.3	12.9	105
Ni	8.73	9.02	103	6.72	8.14	121	8.88	7.94	89	9.14	7.82	86
P	35.3	9.08	26	26.5	22.1	98	26.7	6.91	26	29.4	10.9	37
Pb	22.6	9.61	43	20.9	6.97	33	21.0	5.40	26	19.3	8.94	46
Sb	<5.0	4.72	??	<5.0	1.50	??	<5.0	<0	<0	<5.0	8.29	>100
Se	1.88	1.96	104	2.56	2.51	98	2.99	1.45	49	2.72	2.57	94
V	78.2	53.1	68	83.5	46.7	56	82.6	55.6	67	97.3	59.1	61

Table 47
Recovery of Coal Trace Elements in Flue Gas at the ESP Inlet — Baseline Testing, NAA Analysis, September 1991

	9/18/91			9/19/91			9/20/91			9/21/92		
	Flux, g/min		Recovery, %	Flux, g/min		Recovery, %	Flux, g/min		Recovery, %	Flux, g/min		Recovery, %
	Coal	Gas		Coal	Gas		Coal	Gas		Coal	Gas	
As	5.0	2.32	46	6.4	2.39	37	5.1	2.95	58	4.8	3.46	72
Ba	78	40.0	51	55	40.3	73	74	35.0	47	67	42.6	64
Co	3.4	2.10	62	4.3	2.66	62	4.0	2.81	70	3.5	3.10	89
Cr	19	15.0	79	23	17.6	77	27	16.2	60	19	19.2	101
Hg	<0.051	<0.004	??	<0.049	<0.004	??	<0.068	<0.004	??	<0.058	<0.004	??
Mn	30	16.9	56	80	19.2	24	32	19.5	61	23	21.0	92
Mo	9.5	7.27	77	12	7.05	59	14	7.71	55	9.0	8.57	95
Ni	<14	7.73	??	<14	12.6	??	17	9.18	54	<14	10.4	??
Sb	1.3	1.02	79	1.5	0.89	59	1.8	0.98	55	1.5	1.12	75
Se	2.6	0.14	6	2.5	0.16	6	3.4	0.19	6	3.1	0.21	7
V	53	44.0	83	36	41.3	115	129	47.3	37	51	52.1	102

Table 48
Recovery of Coal Trace Elements in Flue Gas at the ESP Inlet – Low-NO$_x$ Testing, NAA Analysis, January 1992

	1/14/92			1/15/92			1/16/92			1/17/92		
	Flux, g/min		Recov-ery, %	Flux, g/min		Recov-ery, %	Flux, g/min		Recov-ery, %	Flux, g/min		Recov-ery, %
	Coal	Gas		Coal	Gas		Coal	Gas		Coal	Gas	
As	4.2	6.57	157	4.2	6.36	150	4.9	5.44	110	4.7	6.67	140
Ba	76	51.9	68	73	44.9	62	67	42.4	64	64	47.8	74
Co	3.2	2.57	80	3.0	2.09	70	3.0	2.07	70	3.1	2.31	75
Cr	20	17.9	90	21	15.7	75	21	16.9	80	22	17.3	78
Hg	<0.039	<0.003	??	<0.038	<0.003	??	<0.047	<0.003	??	<0.036	<0.003	??
Mn	24.1	19.6	81	22.5	14.6	65	22.7	16.5	73	25.8	17.5	68
Mo	13.4	11.8	88	13.4	11.8	88	12.6	12.3	98	12.3	13.3	108
Ni	<18	10.7	??	<20	6.00	??	<19	6.7	??	<20	11.2	??
Sb	1.8	2.5	140	1.9	2.58	140	2.0	2.32	120	1.7	2.67	150
Se	2.17	1.44	67	0.82	1.94	240	2.99	1.41	47	2.72	1.06	39
V	97	74.1	76	90	70.8	78	93	82.5	89	103	79.1	77

Table 49
Recovery of Mercury from the Coal in Flue Gas at the ESP Outlet (data based on samples collected on sorption tubes)

	Flux, g/min	
	Based on coal analysis (CVAAS)	Based on gas analysis (AFS)[a]
Baseline testing		
Sept. 18	0.078	0.076
Sept. 19	0.088	0.088
Sept. 20	0.087	0.103
Sept. 21	0.076	0.102
Average	0.082 ± 0.006	0.092 ± 0.013
Low-NO_x		
Jan. 14	0.167	0.073
Jan. 15	0.084	0.078
Jan. 16	0.033	0.047
Jan. 17	0.094	0.100
Average	0.094 ± 0.055	0.075 ± 0.022

[a] AFS = atomic fluorescence spectrometry (performed at Brooks Rand, Ltd.).

Table 50
Material Balance Across the ESP System During Baseline Testing

	Element fluxes in gas streams, g/min			Element accumulation rate in hoppers,[c] g/min	Closure, %
	Inlet[a]	Outlet[a]	Net[a,b]		
As	2.15	0.017	2.13	2.82	132
Ba	23.1	0.056	23.0	38.5	60
Be	0.668	<0.008	0.668	<0.972	>69
Cd	1.39[d]	<0.015	1.39	1.47	95
Co	1.90	<0.074	1.90	2.23	117
Cr	11.3	0.124	11.2	14.6	131
Cu	5.07	0.066	5.00	5.47	109
Hg	0.007	<0.001	0.007	<0.004	<57
Mn	15.9[d]	0.075	15.8	18.1	114
Mo	7.14	<0.086	7.14	7.65	107
Ni	7.75	<0.083	7.75	9.12	118
P	13.2	<0.153	13.2	14.9	113
Pb	13.3	<0.115	13.3	13.1	99
Sb	1.40	<0.115	1.40	<0.56	<40
Se	0.286	0.209	0.077	<0.080	??
V	42.9	<0.180	42.9	47.5	111

[a] Flow rate, inlet: 10,998 Nm^3/min
outlet: 10,943 Nm^3/min

[b] Ash concentration: inlet, 7.28 g/Nm^3
outlet, 0.0384 g/Nm^3

[c] Hopper ash accumulation rate: 79,645 g/min

[d] Average of three, not four, results.

Table 51
Material Balance Across the ESP System During Low-NO_x Testing

	Element fluxes in gas streams, g/min			Element accumulation rate in hoppers,[c] g/min	Closure, %
	Inlet[a]	Outlet[a]	Net[a,b]		
As	0.967	0.143	0.824	1.33	161
Ba	79.1	0.276	78.8	39.5	200
Be	0.682	<0.009	0.682	0.248	36
Cd	1.01[d]	<0.033	1.01	2.13	211
Co	2.05	0.64	1.41	1.87	133
Cr	10.6	0.325	10.3	13.8	134
Cu	5.18	<0.015	5.18	5.41	104
Hg	0.016	<0.006	0.016	<0.005	<30
Mn	15.0	1.57[d]	13.4	16.5	123
Mo	10.2	<0.521	9.68	8.63	89
Ni	8.14	<0.111	8.14	8.30	102
P	11.9	0.752	11.1	14.8	133
Pb	7.60	0.232[d]	7.37	10.2	138
Sb	0.944[e]	<0.033	0.944	0.898	95
Se	1.39	0.402	0.988	0.045	5
V	53.1	0.557	52.5	64.4	123

[a] Flow rate, inlet: 10,941 Nm^3/min
outlet: 11,086 Nm^3/min

[b] Ash concentration, inlet: 7.73 g/Nm^3
outlet: 0.0790 g/Nm^3

[c] Hopper ash accumulation rate: 84,486 g/min

[d] Average of three, not four, results

[e] Average of two results.

7. DISCUSSION

The Institute investigators embarked on the investigation at Site 110 with prior experience on the analytical methods in a less complex environment — the relatively clean emissions from the U.S. Army's incineration process for obsolete chemical emissions. Experience from this study led to unexpected findings about the difficulty of following the established methods with the types of emissions that occur with a coal-fired boiler. This discussion is devoted to the problems of completing the assigned tasks at the test site with these methods; it also gives suggestions for improvements in sampling and analysis.

Trace elements. The results obtained on analyses of ash samples by ICP and supporting AAS procedures were disappointing. The impression received in this investigation is that the analytical protocol consisting of acid digestion of ash and analysis of the resulting solution by ICP/AAS methods cannot be used to achieve the desired results without great labor and great risk of error.

The problem begins with the acid digestion procedure described for the work-up of samples from the Multiple Metals Train. Perhaps the procedure was devised for materials other than the fly ash from coal combustion. Certainly, the digestion procedure cannot be depended upon to dissolve all ash samples completely, and it provides no precaution for testing to establish that complete dissolution of the mineral portion occurs, which is critical. The procedure says simply to filter the residue from digestion and proceed with the analysis. Usually, ash will contain unburned carbon that need not be dissolved, but the ash will mask mineral matter that has not been dissolved and that in the absence of contrary evidence must be expected to contain elements that are among the targets for analysis.

The instructions for ICP analysis in Method 6010 emphasize that aluminum and iron will cause interference in the determination of some of the trace elements of interest. They even suggest that a solution may have to be diluted until these two metals are below 50 μg/mL before analysis can proceed. Fly ash from the combustion of coal may easily contain aluminum and iron at concentrations of 10% by weight. If the ash contains 10 μg/g of a trace element, the solution will contain 0.005 μg/mL of that element when aluminum and iron are diluted as directed, and the determination of the element will be jeopardized or made impossible. The instructions call for use of the method of additions to cope with media effects, such as those associated with the common, more concentrated elements. It is doubtful that this provision will make reliable determinations possible for all the elements of concern, notably arsenic and selenium.

The cumulative effect of analytical problems such as those described above makes achieving material balance a very formidable task. If the analyst achieves a reasonable degree of success in the analysis of one stream, with an element determined within a range of ±20% of the true value, but then faces the reality of uncertainties of ±20% in the concentration of that element in each other stream of concern, success in making a meaningful overall material balance will be doubtful at best.

Analytical approaches that were employed for support of the ICP and AAS methods showed promise for becoming preferred methods. In the realm of sampling, the sorption traps for mercury proved to be highly attractive. Insofar as analysis is concerned, neutron activation proved effective for accuracy. Although the cost seems high (the cost was $250 per sample in this work), the cost conceivably is not only competitive but advantageous from the point of view of improved productivity and accuracy. For those elements not determined by NAA, x-ray fluorescence may be an acceptable supplemental method.

Acid gases. The use of the acid gases train was reasonably successful. The samples obtained with this train provided acceptable data in terms of the recovery of the sulfur and halogens in the coal.

Perhaps this train is bulkier than it needs to be, and it seems to be designed for sample volumes that are larger than they need to be. The more simple controlled condensation train yielded superior data for SO_2 in terms of reproducibility and, of course, it also provided data on SO_3. This was done with samples of 0.085 Nm^3, compared with samples of the order of 0.5 Nm^3 with the Acid Gases Train. With somewhat longer sampling times, the controlled condensation train could permit determination of HCl and also HF. It could simultaneously collect ammonia. Possibly it could also collect HCN if the impingers contained a metal ion for complexing cyanide, holding it in solution and protecting it against oxidation by the peroxide that is used in the collection of SO_2.

Aldehydes and ketones. The determination of these compounds seemed straightforward and successful during the second series of sampling experiments in the field. The failure to obtain acceptable data during the first test occasion is a reflection on the judgment of the laboratory analyst. It does not suggest that the sampling method employed or the analytical procedure intended was flawed.

Volatile organics. The quality of the data on volatile organics is uncertain. There are many questions about the quality and reliability of the data. On the critical question, whether benzene and toluene were emitted at significant levels, the answer has to be a qualified yes, although the concentration range is questionable. From a broader perspective, the analysis reveals that if benzene and toluene are indeed significant emissions, there is a much wider variety of compounds emitted, whose identities were not established.

The sampling and analytical techniques were clearly flawed during the baseline test series. The evidence for this is the large number of contaminants (or presumed contaminants) that were encountered sporadically at highly variable concentrations. There was improvement in technique during the low-NO_x series; the number of contaminants was reduced. Still, there were apparent variations in the concentrations of those substances believed to be actual components of the flue gas that cannot be explained on a rational basis. Why should the apparent concentration of benzene be zero in one sampling operation, and another be 10,000 $\mu g/Nm^3$ under nominally the same conditions? Instances of such variations were encountered during test series.

The total hydrocarbon analyzer in service at the plant rarely recorded concentrations above 0.55 ppmv and typically recorded concentrations between 0.05 and 0.55 ppmv. The reliability of this instrument is not known. If, however, the benzene concentration had ever reached 10,000 $\mu g/Nm^3$ (3 ppmv), the instrument should have shown a response above the range consistently recorded. THC instruments are usually calibrated with propane. The responses to different hydrocarbons at equal concentrations will differ, but most THC analyzers will give a response to benzene that is greater than that to propane at the same concentration. Episodes when elevated readings occurred (above the typical range of 0.5 to 0.55 ppmv) were extremely rare and brief; one such unusual episode occurred on January 14 when successive readings at 5-min intervals were 0.15, 43.85, 79.45, -0.25, -0.05, and 0.15 ppmv. The duration of this particular upset was long enough to have profoundly affected any sample being simultaneously collected with the VOST. Such upsets were too rare, on the other hand, to have produced all the questionable data on benzene that VOST yielded.

The literature available for review fails to support the finding of benzene concentrations as high as those found in this work. Garcia et al. (12) gave the following concentrations as typical of emissions from coal-fired power plants:

Benzene	14 μg/Nm^3
Toluene	119 μg/Nm^3
Ethylbenzene	21 μg/Nm^3
Xylenes (all three)	80 μg/Nm^3

This absolute concentration of benzene and the concentrations of the other compounds that are higher than that of benzene differ from the results of this work.

Ahlberg et al. (13) reported somewhat higher benzene concentrations from coal-fired boilers, near 100 μg/Nm^3. Still, the difference between this level and the maximum level found in this work is a factor of 100.

Logan et al. (14) reported difficulties with benzene in their validation of the VOST. These authors refer to "the inherent problem of benzene contamination in the Tenax sorbent." They cite recoveries of 300%, but at concentrations far below those sometimes encountered in this work. The basis for the reference to the inherent problem with benzene is not explained; the reference, however, may have to do with the fact that the Tenax polymer is a phenylene oxide polymer that has susceptibility to attack by vigorous reactants, such as NO$_x$. Benzene is a possible product of such an attack. Unfortunately, the procedures with blanks that are part of the VOST procedure do not allow evaluation of the effects on the sorbent of reactants in the gas stream.

Recent solicitations for air toxics work have sometimes required only benzene and toluene to be determined. It is doubtful that the broad potential of the VOST procedure justifies the cost of this procedure if data on just benzene and toluene are required. On the other hand, in view of the long list of target compounds in the 1990 Clean Air Act Amendments that may be determined by the VOST procedure, one must question whether data only on benzene and toluene are sufficient.

Semi-volatile organic compounds. The information obtained on semi-volatile compounds indicates that this class of compounds is a less serious form of emissions than the volatiles. The target PAH compounds except naphthalene did not occur at measurable concentrations, and naphthalene was observed only sporadically. Other compounds on an extended list of targets were found at much lower concentrations than benzene and are thus less a cause of disturbance.

There is another less complacent viewpoint on the results for semi-volatiles. The appearance of a large number of unidentified semi-volatiles during low-NO_x firing, at elevated concentrations, indicates that low-NO_x firing does have an undesirable impact on emissions. Prudence will require that they ultimately be identified.

8. CONCLUSIONS

This final technical discussion will be focussed on the answers that can be offered on the key questions of concern:

1) How does the change to low-NO_x firing alter the emission of hazardous air pollutants?

2) What degree of control over the emission of air toxics is exercised by the hot-side ESP?

3) What added benefit toward the control of emissions does the cold-side ESP provide?

Effect of low-NO_x firing. As far as inorganic emissions are concerned, there was no clear-cut effect from low-NO_x firing. In this statement, the term inorganics refers to the trace elements collected with the Multiple Metals Train and the SO_x, HF, and HCl collected with the Acid Gases Train.

If there were effects on the emissions of the trace elements, the effects were too subtle to be detected in the scattered analytical data. To be sure, if the data are examined superficially, differences will be seen between the results of the baseline and low-NO_x test series. For example, arsenic was found at lower concentrations in the gas stream during the latter testing. The explanation must be presumed to lie in the problems of analysis, not in an actual change brought about by the firing change. Certainly, an important aspect of the emission of trace metals to the environment concerns the emission of metal vapors, which escape control by electrostatic precipitation. Arsenic does not exist to a large degree as a vapor. The two elements that do exist significantly as vapor are mercury and selenium. The measured emission of mercury was somewhat lower with low-NO_x firing and that of selenium was somewhat higher in that mode. Still, neither emission can be said to be different in the two firing modes because of the uncertainties in the analytical results.

Analysis of the data on inorganics to detect the effects of the firing change is handicapped not only by the scatter in the analytical data but by the absence of anticipated effects that could be looked for specifically. One mechanism that might be responsible for changes would be a shift in the temperature profile in the furnace and a corresponding effect on element volatilities. Another mechanism might be the suppression of oxidizing conditions, which could shift the proportions of an element in different oxidation states, such as Cr(III) and Cr(VI) or As(III) and As(V). There is indeed an indication in some of the data (but not all) that the reduced state As(III) was enhanced, (an undesirable change) and a further, more definite indication that the oxidized state Cr(VI) was suppressed (a desirable effect.)

Emissions of SO_x, HF, and HCl seem to have been unaffected by the change in firing conditions. Emissions of ammonia and HCN perhaps are more relevant to the shift to low-NO_x firing, because both contain the element nitrogen in reduced states in contrast to the oxidized states present in NO_x. Both ammonia and HCN were found at low concentrations in both the baseline and low-NO_x test series but at lower concentrations in the latter, where increases might have been logical.

With respect to organic emissions, the experimental findings can be summarized as follows:

- No effect on aldehydes and ketones was detected because an analytical error destroyed the samples from the baseline testing without yielding any acceptable data.

- The concentrations of benzene and toluene, if altered, were reduced by the shift to low-NO_x firing. This change seems improbable and may reflect the uncertain quality of the data obtained. The occurrence of other detectable volatile organics was suppressed by the shift in firing conditions, but this change is believed to be due to the exclusion of contaminants or other interfering substances, not due to the shift in firing conditions. There was generally less material in the category of unidentified volatiles during the low-NO_x firing.

- The concentrations of identifiable PAH compounds, the primary analytical targets, were not significantly altered by low-NO_x firing. PAHs on the target list were mostly absent or below the detection limits. The amount of total organic matter detectable as semi-volatile compounds, on the other hand, appeared to be substantially increased with the change in firing mode. None of the individual compounds involved in this increase was identified.

Effect of the hot-side ESP. The effect of the hot-side ESP on emission of the trace elements was discussed by reference to the penetration data in Table 24. The penetration of most of the elements was within the range 1 to 5%. The exceptions with higher penetrations were the volatile metals, mercury and selenium.

It is paradoxical that the penetrations are as high as the values mentioned above when most of the elements occur primarily in the particulate matter and the penetration of the total particulate matter is approximately 0.5%. This paradox raises two important questions: Are very few of the trace elements primary components of the aluminosilicate matrix that constitutes the bulk of the fly ash? Do most of the trace elements occur primarily in fine particles that account for most of the mass penetrating the ESP? Unfortunately, these questions cannot be answered from the available data.

Not surprisingly, the hot-side ESP had no measurable influence on the emissions of SO_x, HF, and HCl. The concentrations of these acid gases were the same at the outlet as at the inlet, insofar as can be determined from the scatter in the analytical data.

Quite surprisingly, on the other hand, the ESP seemed to suppress the emission of certain organic substances. Suppression of the emission of formaldehyde is particularly difficult to explain. Whatever mechanism may explain the effect on formaldehyde may explain the effects on other compounds in the vapor state. The effect is hardly precipitation per se; it is more likely to involve a chemical change (probably oxidation) that occurs during residence of the flue gas in the open space of the ESP for several seconds at 700 °F. Although the precipitation of formaldehyde molecules surely does not occur, the postulated chemical change may be induced by the corona regions of the ESP, which provides various high-energy species (electrons, ions, and free radicals, and molecules such as ozone) in the corona regions.

Compounds less volatile than formaldehyde may be indirectly precipitated because they are adsorbed on the surfaces of fly ash particles undergoing direct precipitation. Such compounds presumably make up part of the semi-volatile matter analyzed, which is collected in part on a particulate filter. No such compounds, however, were found on ash removed from the ESP hoppers. The most logical way to explain the two disparate experimental results — first, disappearance of the organics between the inlet and outlet of the ESP and, second, non-appearance of this material in the hopper ash — is that chemical change removes the organic matter while it resides on the ash, which can remain hot for an extended time in the hoppers.

Effect of the cold-side ESP. Obtaining data with the cold-side ESP in operation only one day in each four-day test period made it difficult to detect any but the most emphatic effect of that ESP. No dramatic effect was seen. Little effect, if any, occurred in the control of total particulate matter. The main place then to search for reduced emissions would be for materials that are volatile at the hot-side temperature but not volatile at the cold-side ESP. Such materials are mercury and selenium. Improved control of these trace elements was not observed.

REFERENCES

1. W. Chow. "PISCES: Tracking Trace Chemicals in Power Plants." J. Air Waste Manage. Assoc. 40, 806 (1990).

2. B. Lee. "Highlights of the Clean Air Act Amendments of 1990." J. Air Waste Manage. Assoc. 41, 16 (1991).

3. D. J. Boron and E. I. Wan. "Controlling Toxic Emissions." Coal, 96 (6), 121 (1990).

4. J. P. Gooch, R. E. Bickelhaupt, G. H. Marchant, Jr., R. D. McRanie, L. E. Sparks, and R. F. Altman. "Improvement of Hot-side Precipitator Performance with Sodium Conditioning." J. Air. Pollut. Contr. Assoc. 31, 291 (1981).

5. Test Methods for Evaluating Solid Waste. EPA/SW-846, Third Edition, November 1986 (published in Volumes IA, IB, IC, and II).

6. S. Garg (Work Assignment Manager). "Methods Manual for Compliance with the BIF Regulations." EPA/530-SW-91-010, December 1990.

7. Generic Sampling and Analytical Plan — Field Chemical Emissions Monitoring, manual prepared by Radian Corporation for the Electric Power Research Institute. EPRI Project RP 3177-1, August 31, 1990.

8. Nicolas S. Bloom. "Chemical Speciation of Mercury in Coal Fired Powerplant Stack Gases — Overcoming the Analytical Problems." Managing Hazardous Air Pollutants: State of the Art (technical conference), Washington, DC, November 4-6, 1991.

9. P. Weigert and A. Sappl. "Speciation of As(III) and As(V) in Biological Tissue." Fresenius Z. Anal. Chem. 316, 306 (1983).

10. R. M. Riggin. "EPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air." EPA 600/4-84-041, April 1984.

11. H. Braun, M. Metzger, and H. Vogg. "New Findings on the Mercury Emissions from Municipal Solid Waster Incineration — Speciation, Mass Balance, and Removal." Chem. Environ., Proc. Conf. 1986 (J. N. Lester, et al., editors), pp 117-122.

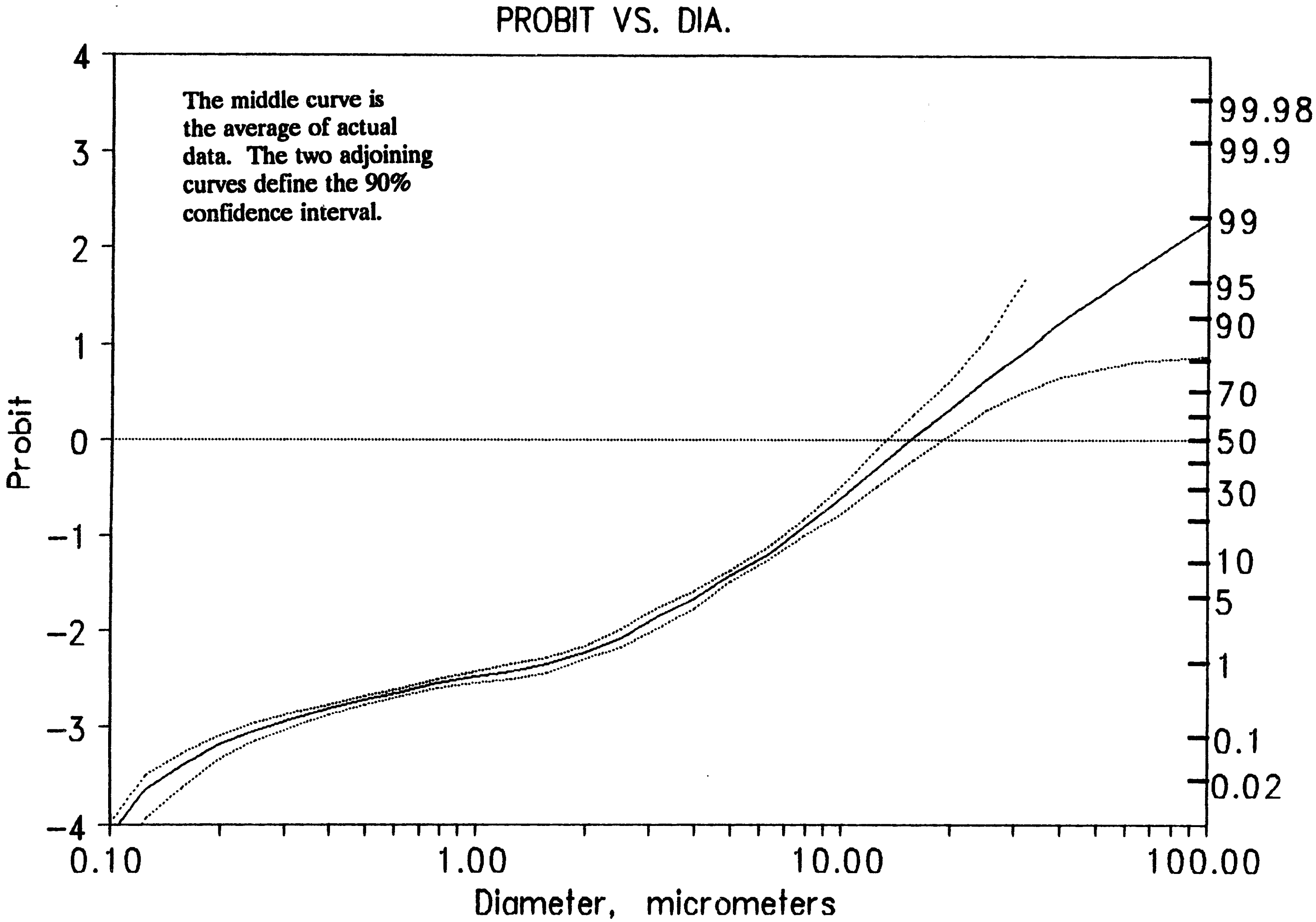
12. J. P. Garcia, S. Beyne-Masclet, G. Mouvier, and P. Masclet. "Emissions of Volatile Organic Compounds by Coal-Fired Power Stations." Atmos. Environ. 26A, 1589 (1992).

13. M. Ahlberg, L. Berghem, G. Nordberg, S. A. Persson, L. Rudling, and B. Steen. "Chemical and Biological Characterization of Emissions from Coal- and Oil-fired Power Plants." Environ. Health Persp. 47, 85 (1983).

14. T. J. Logan, R. G. Fuerst, M. R. Midgett, and J. Prohaska. Validation of the Volatile Organic Sampling Train (VOST) Protocol. Volume II. Field Validation Phase. EPA/600/4-86-1-014b, January 1986.

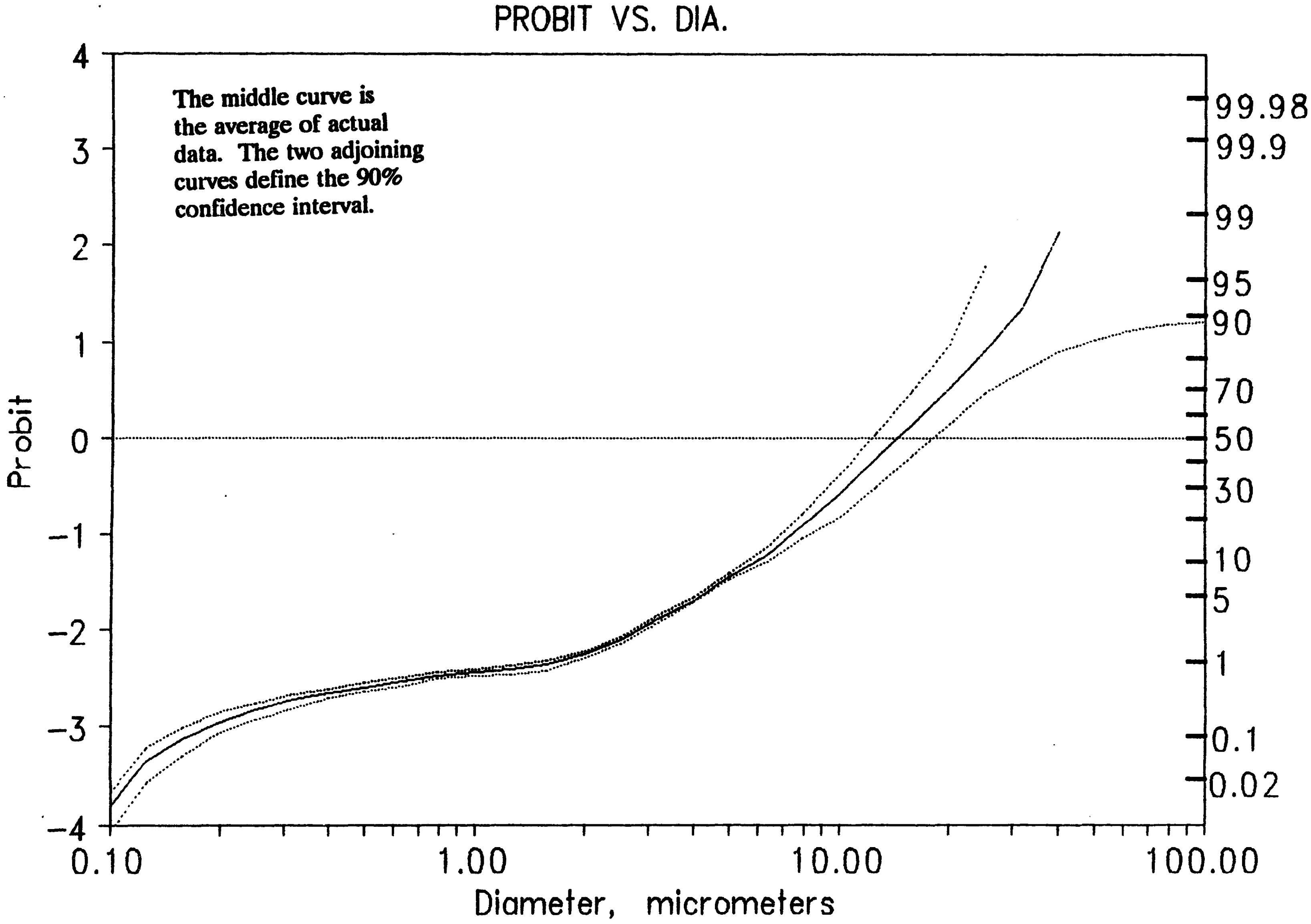
APPENDIX A

GRAPHS OF PARTICLE-SIZE DATA



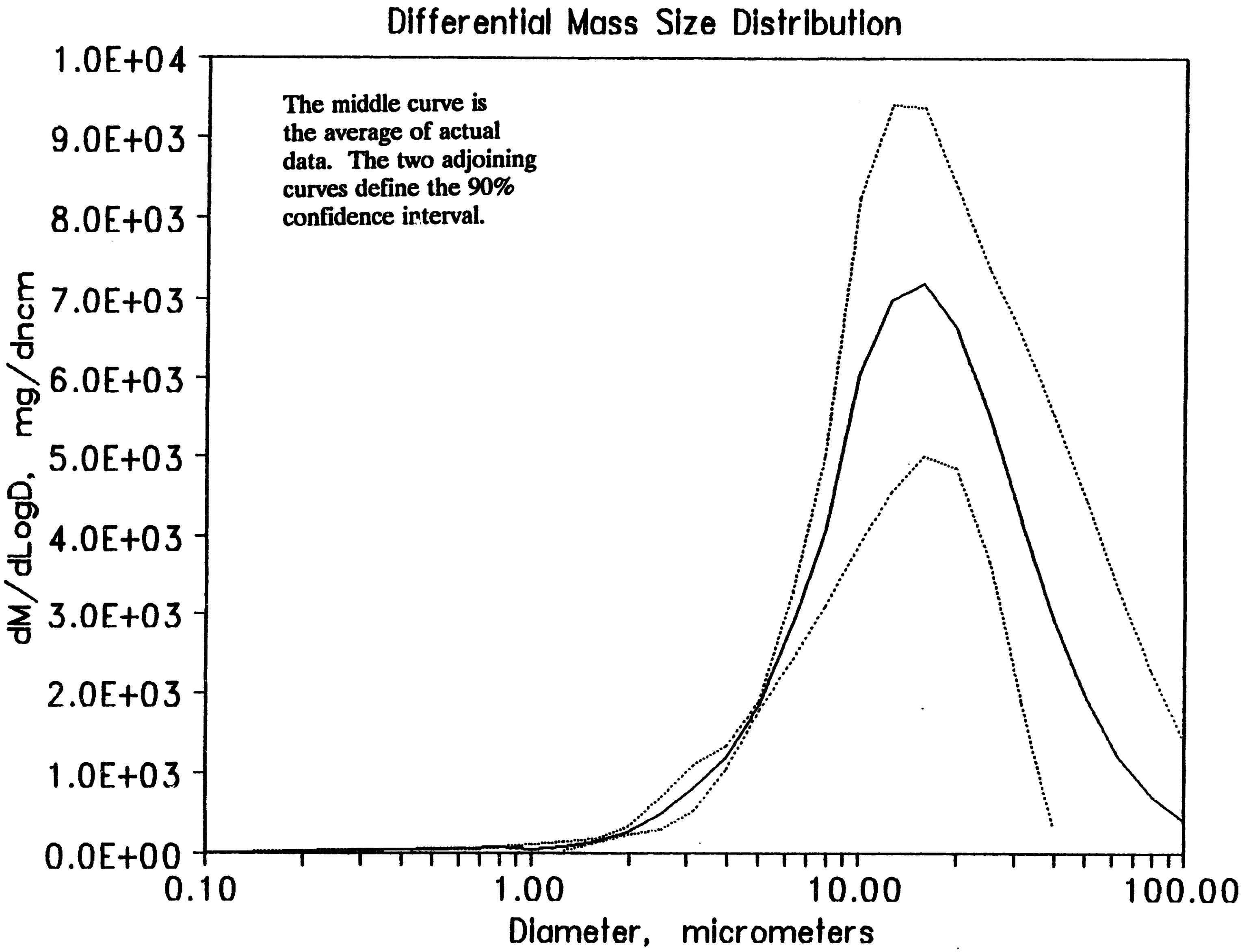
The middle curve is the average of actual data. The two adjoining curves define the 90% confidence interval.

Figure A-1. Cumulative mass versus particle size--baseline testing, ESP inlet.



The middle curve is the average of actual data. The two adjoining curves define the 90% confidence interval.

Figure A-2. Cumulative mass versus particle size--low-NO_x testing, ESP inlet.



The middle curve is the average of actual data. The two adjoining curves define the 90% confidence interval.

Figure A-3. Differential concentration versus particle size--baseline testing, ESP inlet.

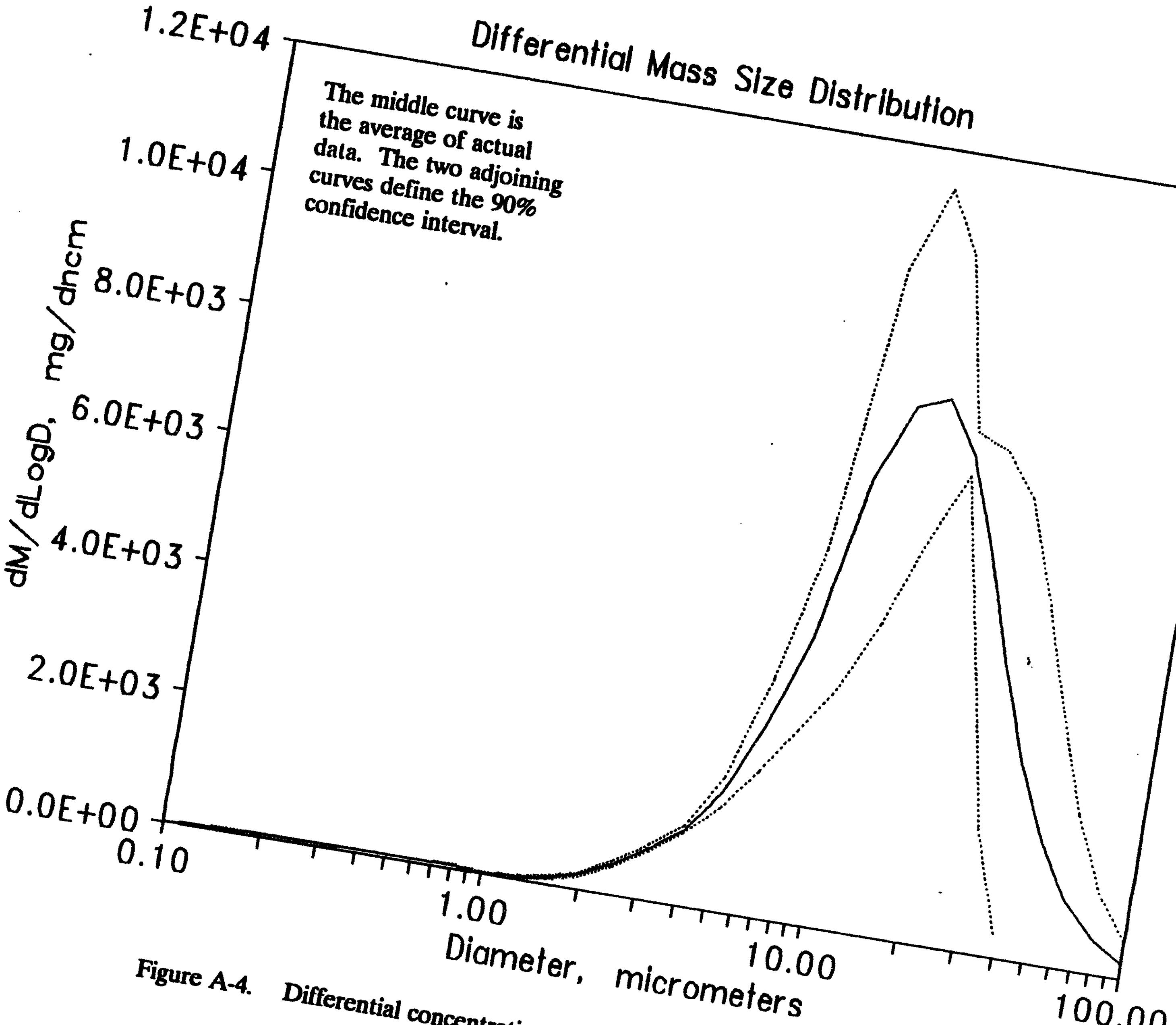


Figure A-4. Differential concentration versus particle size--low-NO_x testing, ESP inlet.

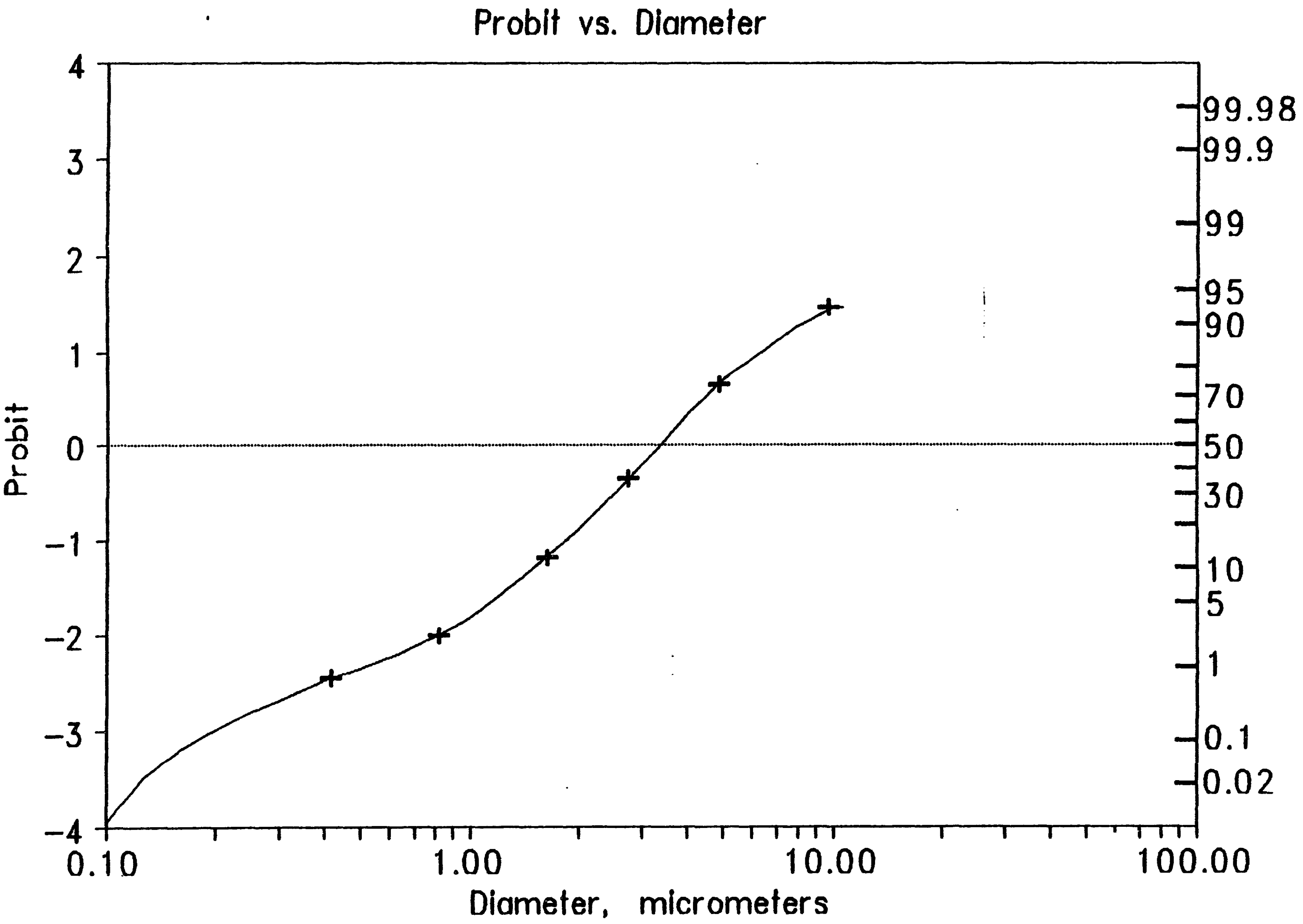


Figure A-5. Cumulative mass versus particle size--baseline testing, ESP outlet with cold-side ESP energized.

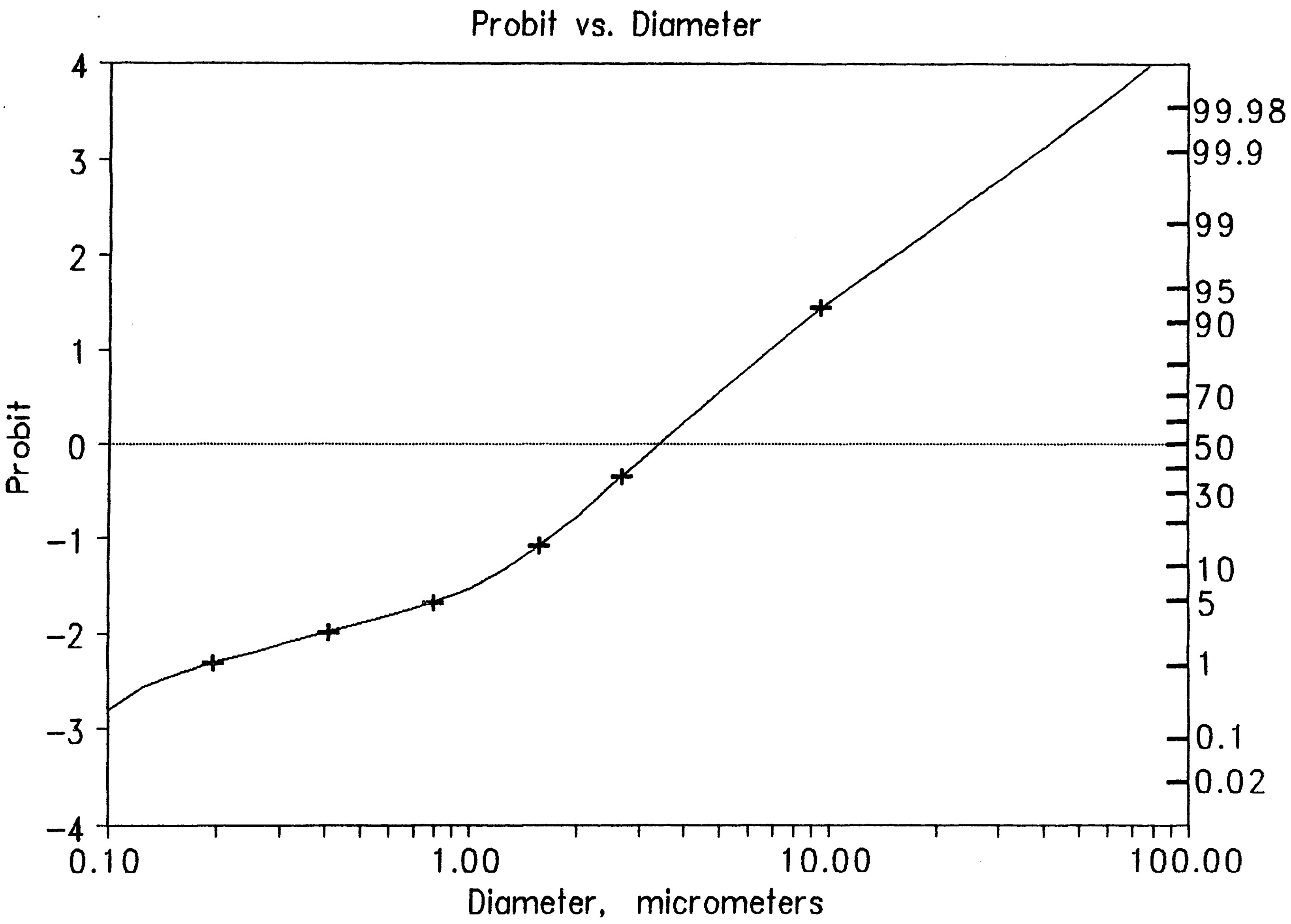


Figure A-6. **Cumulative mass versus particle size--low-NO$_x$ testing, ESP outlet with cold-side ESP energized.**

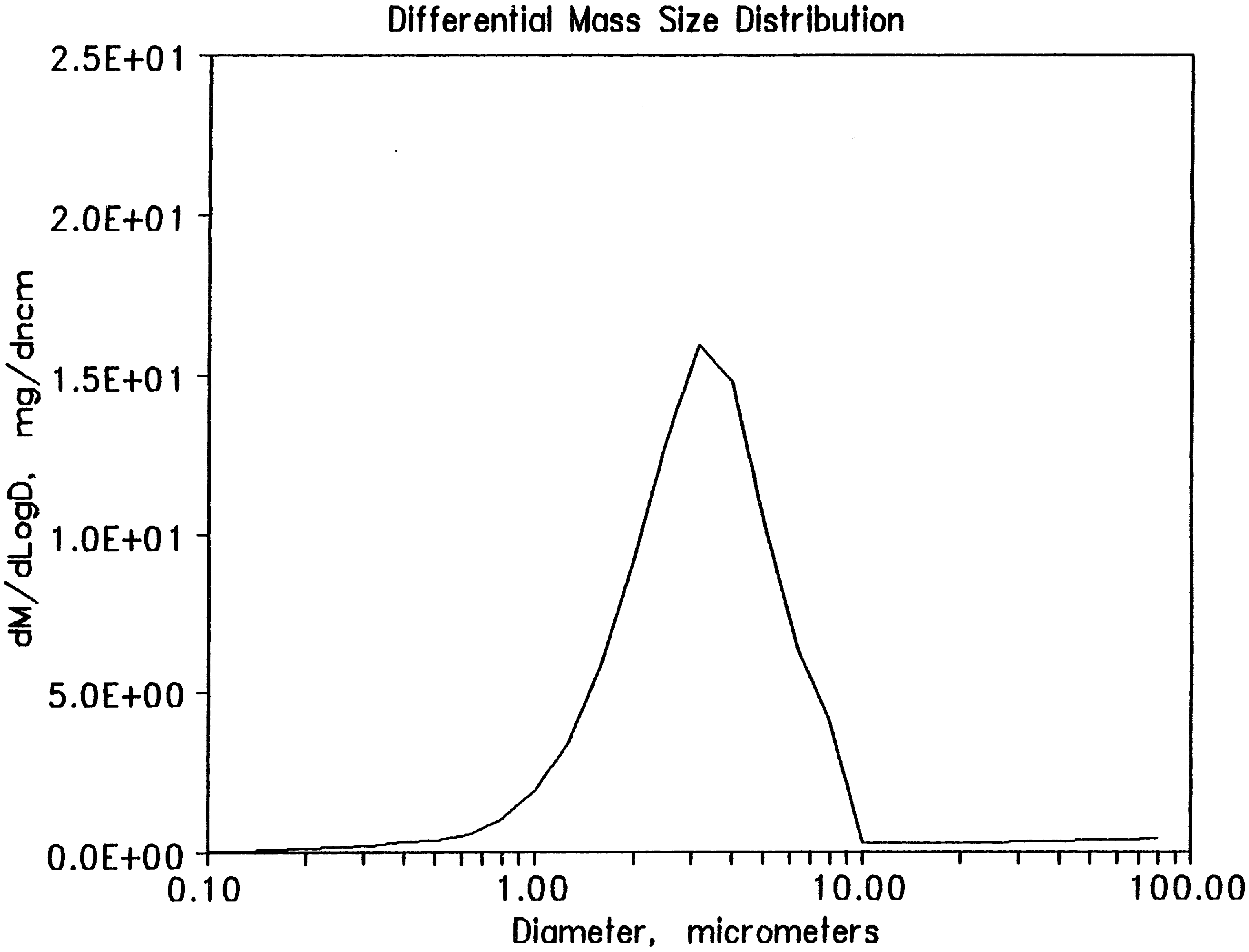


Figure A-7. Differential concentration versus particle size--baseline testing, ESP inlet with cold-side ESP energized.

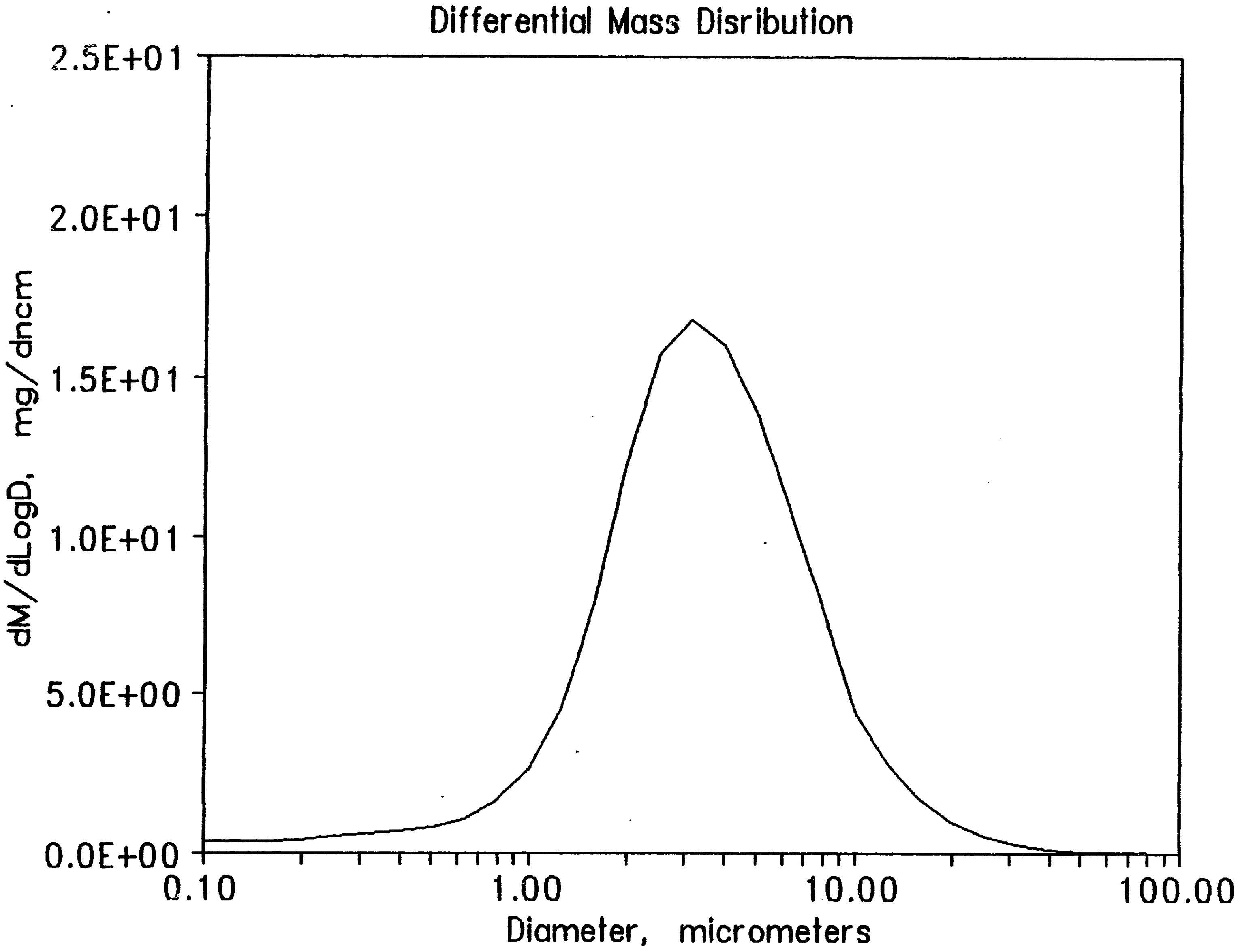
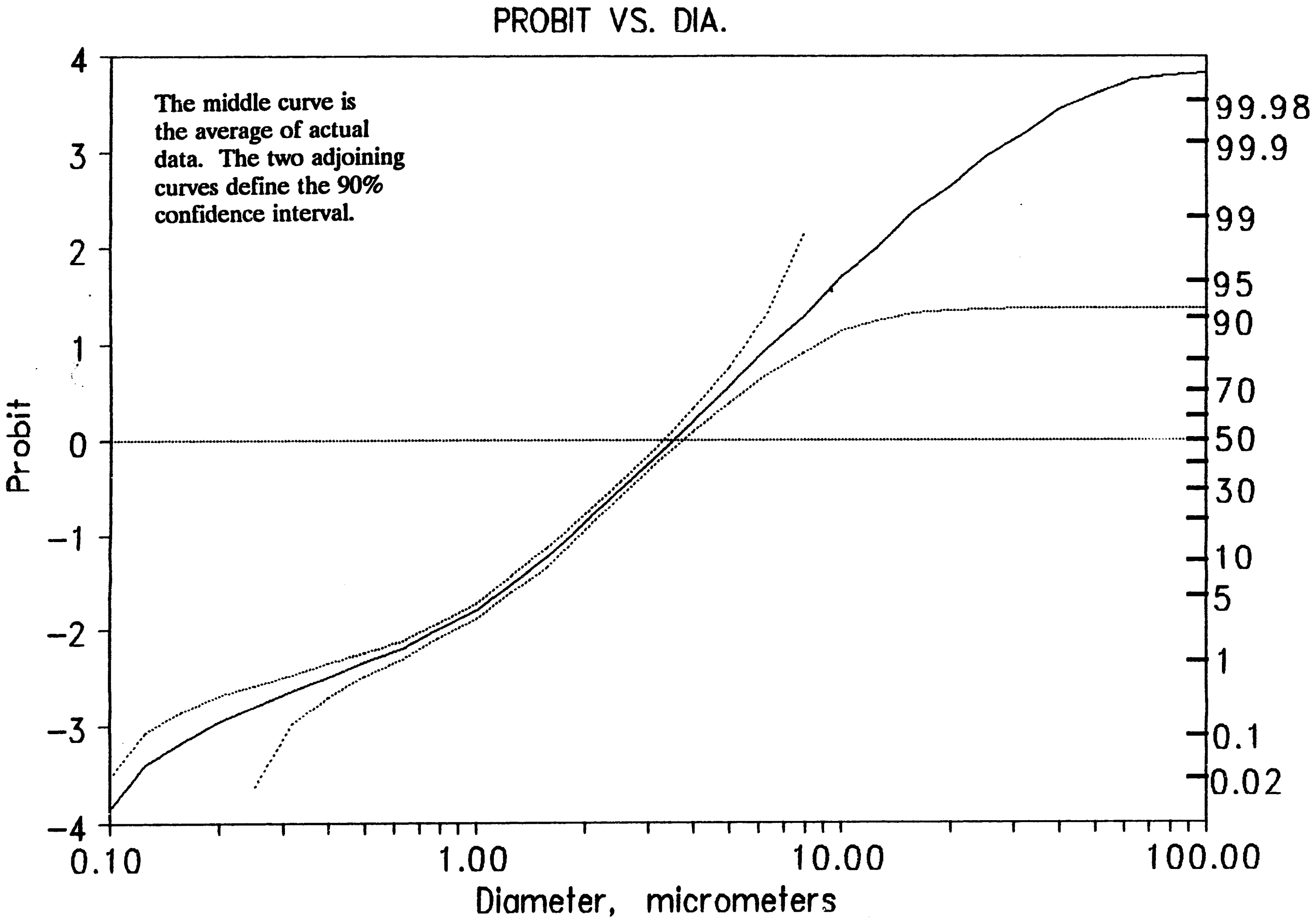
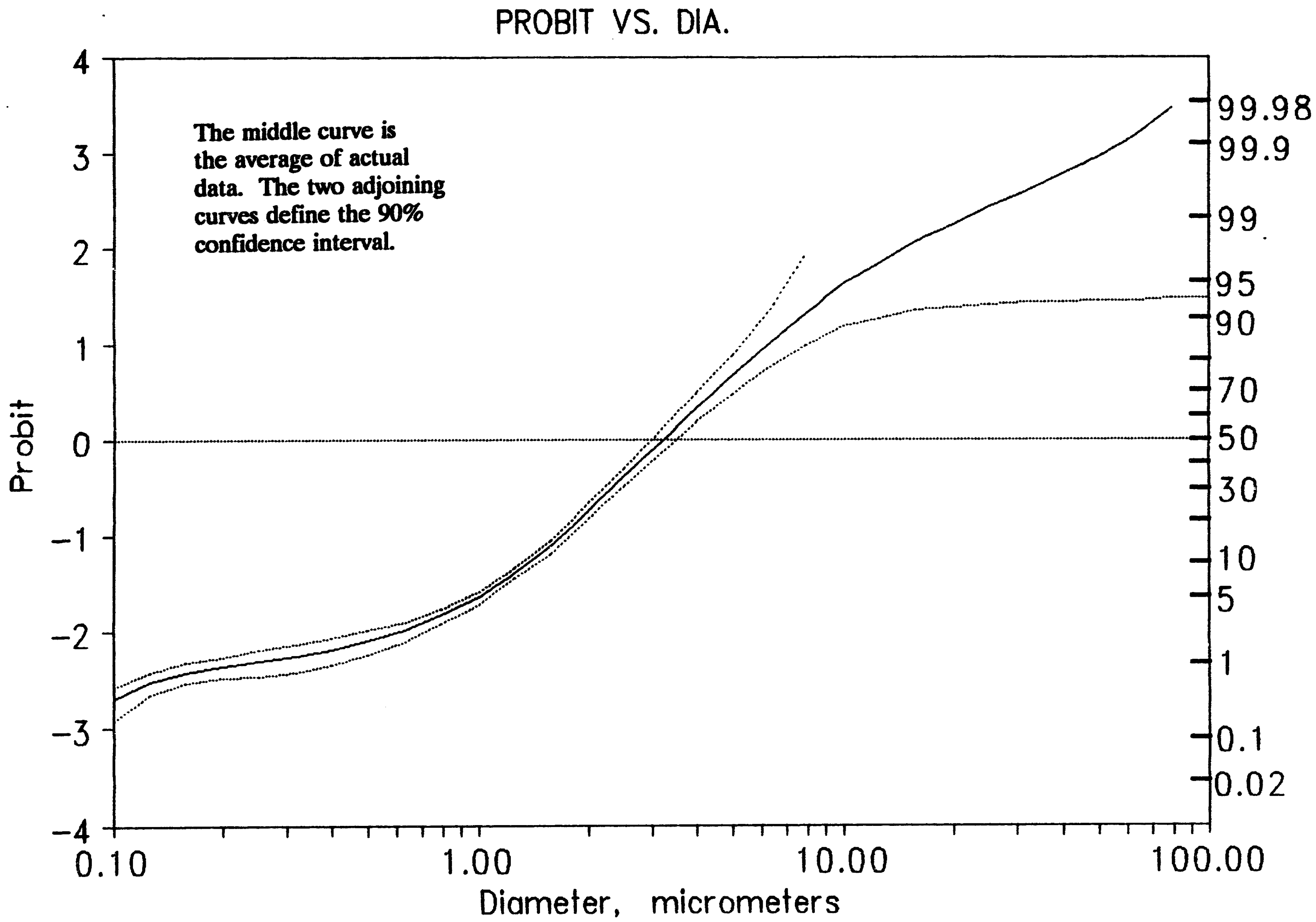


Figure A-8. Differential concentration versus particle size--low-NO_x testing, ESP inlet with cold-side ESP energized.



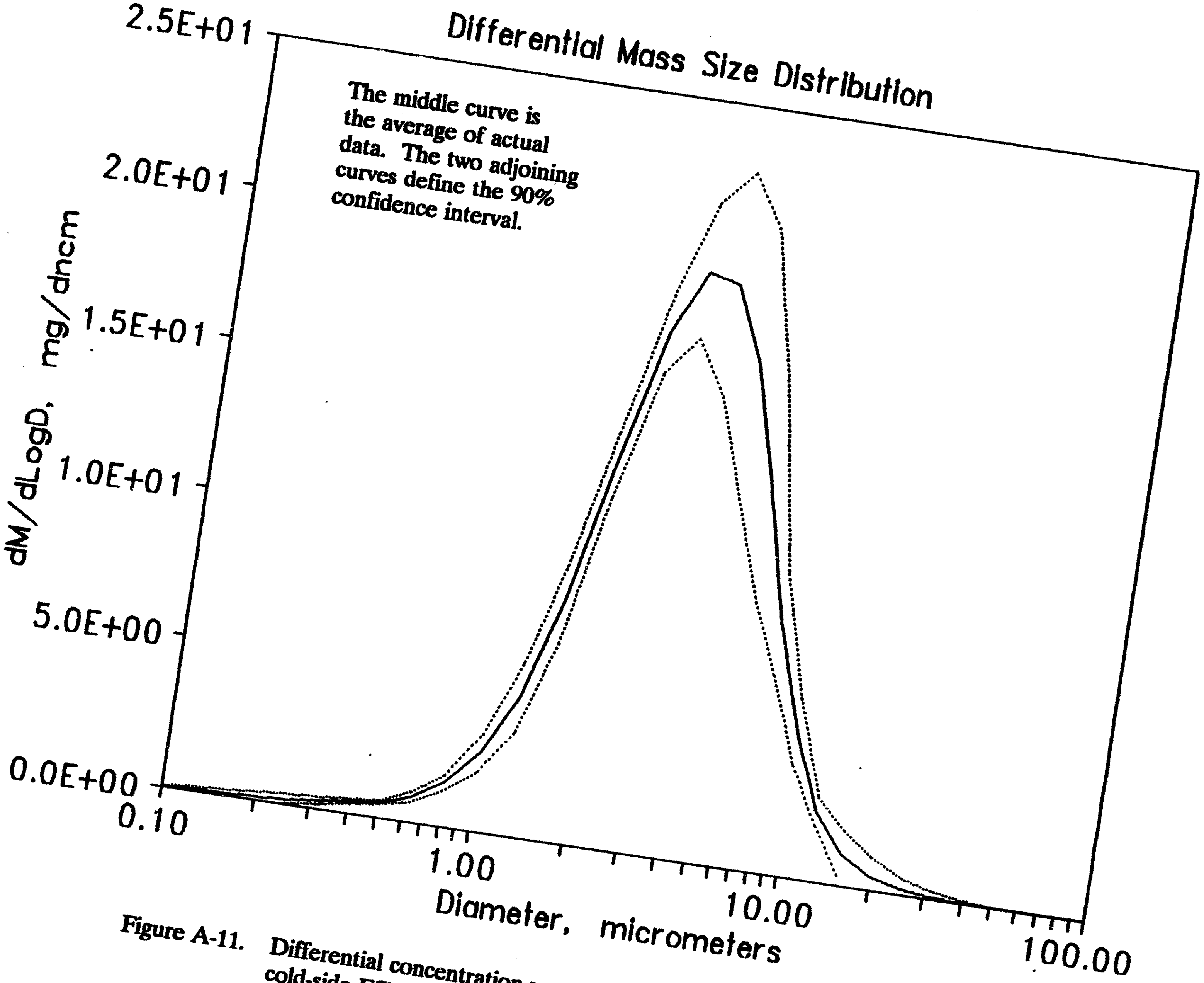
The middle curve is the average of actual data. The two adjoining curves define the 90% confidence interval.

Figure A-9. Cumulative mass versus particle size--baseline testing, ESP outlet with cold-side ESP not operating.



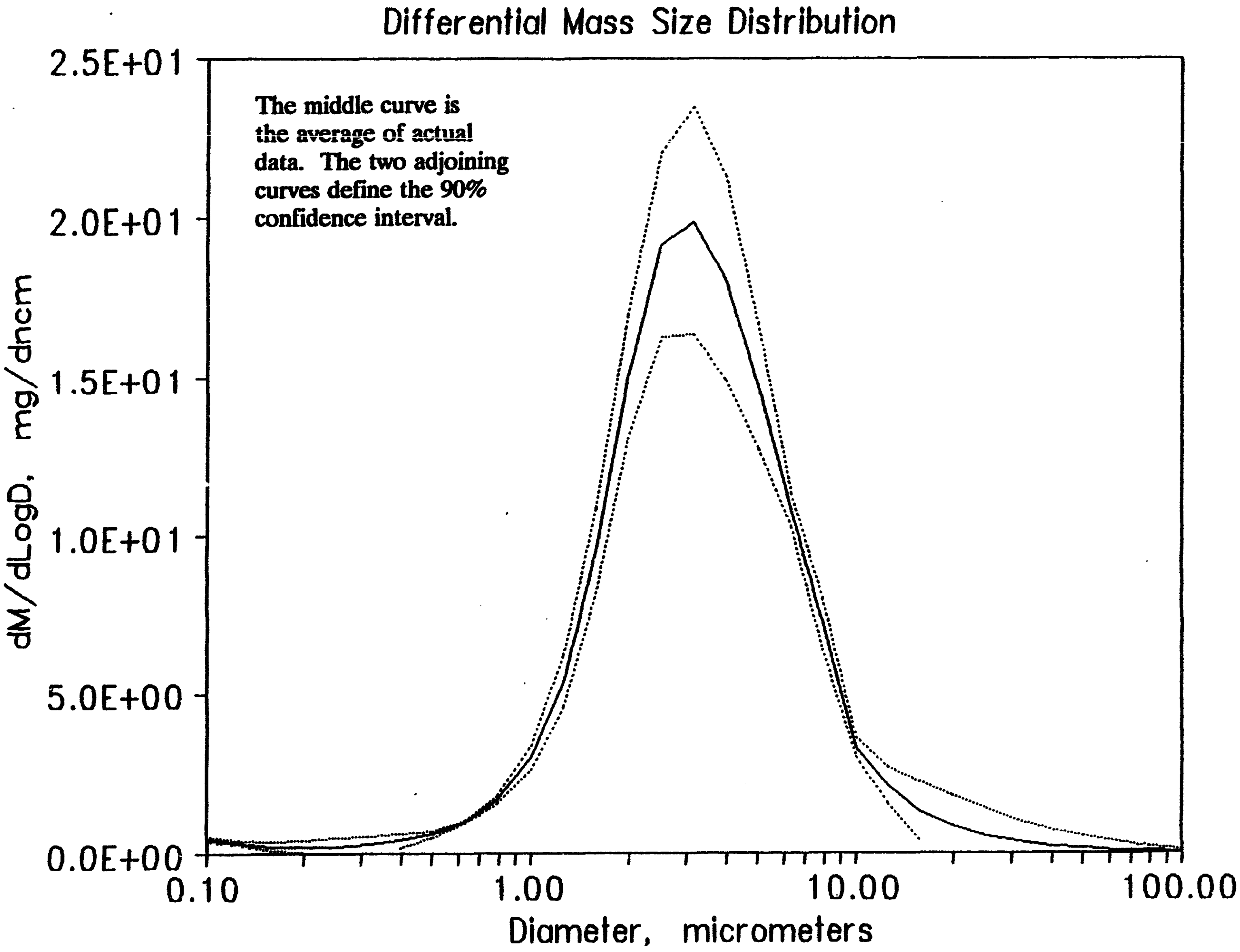
The middle curve is the average of actual data. The two adjoining curves define the 90% confidence interval.

Figure A-10. Cumulative mass versus particle size--low-NO_x testing, ESP outlet with cold-side ESP not operating.



The middle curve is the average of actual data. The two adjoining curves define the 90% confidence interval.

Figure A-11. Differential concentration versus particle size--baseline testing, ESP outlet with cold-side ESP not operating.



The middle curve is the average of actual data. The two adjoining curves define the 90% confidence interval.

Figure A-12. Differential concentration versus particle size--low-NO_x testing, ESP outlet with cold-side ESP not operating.

APPENDIX B

CORRESPONDENCE AND DATA
from
Michael D. Glascock
University of Missouri-Columbia

NEUTRON ACTIVATION ANALYSIS

UNIVERSITY OF MISSOURI-COLUMBIA

Research Reactor Facility

Research Park
Columbia, Missouri 65211
Telephone (314) 882-~~4211~~ 527
FAX [314] 882 6360

December 16, 1991

FAX No: 205-581-2875

Edward Dismukes
Southern Research Institute
P.O. Box 55305
Birmingham, AL 35255-5305

Dear Mr. Dismukes:

I have completed the work required to extract the concentrations for Hg, Mo and Se from the coal and ash samples. The data have been enclosed on a tabulation of data for all elements.

I apologize for failing to send these earlier. The analyses were conducted with a larger batch of geological specimens for which we routinely do not report those three elements and as a result Hg, Mo and Se were overlooked. The data for Mo are fine as there are no analytical interferences. However, the data for Hg and Se are more uncertain than other reported elements because of interferences which occur when analyzing for Hg and Se by NAA. In general, the orders of magnitude are okay but the absolute values for Hg and Se are somewhat more uncertain that all other elements reported.

A copy of this letter will be sent by regular mail. If you have any questions, do not hesitate to call.

Sincerely,

Michael D. Glascock

Michael D. Glascock

Enclosure

COLUMBIA KANSAS CITY ROLLA ST. LOUIS

an equal opportunity institution

Table I. Concentrations of Major and Trace Elements in Coal and Ash Samples (December 1991).

Ident.	Al (%)	As (ppm)	Ba (ppm)	Ca (%)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cs (ppm)	Dy (ppm)	Eu (ppm)
SRI-1	0.85	4.0	62	0.42	11	2.7	15	1.0	0.63	0.16
SRI-2	1.00	5.1	44	0.84	10	3.4	18	1.0	0.77	0.18
SRI-3	1.09	4.0	58	0.24	11	3.1	21	1.1	0.80	0.19
SRI-4	0.95	3.7	52	0.24	10	2.7	15	1.0	0.59	0.17
SRI-5	9.70	33.7	580	3.51	99	30.4	217	10.5	6.79	1.73
SRI-6	9.55	30.5	515	3.41	106	34.0	225	10.4	7.29	1.84
SRI-7	10.16	35.7	423	3.21	107	34.0	196	10.6	7.81	1.88
SRI-8	9.89	38.2	470	3.36	106	34.2	212	10.7	7.39	1.85
SRI-11	9.54	40.7	527	3.78	101	30.2	180	9.9	7.29	1.80
SRI-17	9.23	36.9	401	3.70	107	32.0	171	9.9	7.11	1.82

Samples from Site 110, September 1991

SRI-1	Coal, Sept. 18
SRI-2	Coal, Sept. 19
SRI-3	Coal, Sept. 20
SRI-4	Coal, Sept. 21
SRI-5	Cyclone ash, Sept. 18
SRI-6	Cyclone ash, Sept. 19
SRI-7	Cyclone ash, Sept. 20
SRI-8	Cyclone ash, Sept. 21
SRI-11	ESP ash, Sept. 18
SRI-12	ESP ash, Sept. 20

Table I. Concentrations of Major and Trace Elements in Coal and Ash Samples (December 1991).

Ident.	Fe (%)	Hf (ppm)	Hg (ppb)	K (%)	La (ppm)	Lu (ppm)	Mn (ppm)	Mo (ppm)	Na (%)	Nd (ppm)
SRI-1	1.1	0.55	< 41	0.15	5.0	0.11	24	7.6	0.04	5.5
SRI-2	1.2	0.58	< 39	0.21	5.0	0.12	64	9.2	0.03	4.7
SRI-3	1.4	0.57	< 53	0.31	5.0	0.12	25	10.8	0.05	3.8
SRI-4	1.0	0.55	< 45	0.18	4.6	0.10	18	7.0	0.04	4.2
SRI-5	9.8	5.40	< 58	2.15	47.7	1.10	245	105.4	0.40	41.9
SRI-6	11.3	5.56	< 49	2.20	49.0	1.08	243	90.1	0.37	49.6
SRI-7	11.3	5.67	< 49	2.25	51.4	1.08	236	93.3	0.36	49.1
SRI-8	11.1	5.62	< 59	2.25	51.2	1.10	232	94.5	0.36	48.7
SRI-11	11.5	5.52	< 25	2.20	49.1	1.04	247	85.5	0.38	42.9
SRI-17	12.2	5.62	< 32	1.99	49.7	1.03	231	79.2	0.32	48.5

Samples from Site 110, September 1991

SRI-1	Coal, Sept. 18
SRI-2	Coal, Sept. 19
SRI-3	Coal, Sept. 20
SRI-4	Coal, Sept. 21
SRI-5	Cyclone ash, Sept. 18
SRI-6	Cyclone ash, Sept. 19
SRI-7	Cyclone ash, Sept. 20
SRI-8	Cyclone ash, Sept. 21
SRI-11	ESP ash, Sept. 18
SRI-12	ESP ash, Sept. 20

Table I. Concentrations of Major and Trace Elements in Coal and Ash Samples (December 1991).

Ident.	Ni (ppm)	Rb (ppm)	Sb (ppm)	Sc (ppm)	Se (ppm)	Sm (ppm)	Sr (ppm)	Ta (ppm)	Tb (ppm)	Th (ppm)
SRI-1	< 11	13	1.0	2.4	2.1	1.0	< 14	0.13	0.10	1.5
SRI-2	< 11	14	1.2	2.4	2.0	1.1	< 15	0.13	0.12	1.5
SRI-3	13	15	1.4	2.5	2.7	1.1	16	0.14	0.12	1.6
SRI-4	< 11	13	1.2	2.3	2.4	0.9	38	0.14	0.09	1.5
SRI-5	112	145	14.8	23.4	2.1	10.4	191	1.37	1.01	15.4
SRI-6	161	147	11.4	24.1	2.0	10.8	161	1.36	1.13	15.8
SRI-7	111	147	11.9	24.5	2.1	11.2	234	1.36	1.12	16.3
SRI-8	115	142	12.4	24.1	2.3	11.1	274	1.36	1.08	15.8
SRI-11	91	137	14.0	23.4	2.1	10.4	227	1.39	1.04	15.7
SRI-17	83	141	11.9	23.5	2.1	10.7	252	1.33	1.07	15.7

Samples from Site 110, September 1991

SRI-1	Coal, Sept. 18
SRI-2	Coal, Sept. 19
SRI-3	Coal, Sept. 20
SRI-4	Coal, Sept. 21
SRI-5	Cyclone ash, Sept. 18
SRI-6	Cyclone ash, Sept. 19
SRI-7	Cyclone ash, Sept. 20
SRI-8	Cyclone ash, Sept. 21
SRI-11	ESP ash, Sept. 18
SRI-12	ESP ash, Sept. 20

Table I. Concentrations of Major and Trace Elements in Coal and Ash Samples (December 1991).

Ident.	Ti(%)	U(ppm)	V(ppm)	Yb(ppm)	Zn(ppm)	Zr(ppm)
SRI-1	0.04	2.0	42	0.46	17	32
SRI-2	0.05	2.7	29	0.44	17	26
SRI-3	0.07	3.2	101	0.49	19	28
SRI-4	0.06	1.8	40	0.41	25	23
SRI-5	0.56	23.2	638	4.46	400	275
SRI-6	0.55	25.2	528	4.30	372	338
SRI-7	0.54	25.9	572	4.77	418	293
SRI-8	0.53	25.7	575	4.62	472	285
SRI-11	0.57	23.5	628	4.19	373	265
SRI-17	0.50	23.1	542	4.22	376	277

Samples from Site 110, September 1991

SRI-1	Coal, Sept. 18
SRI-2	Coal, Sept. 19
SRI-3	Coal, Sept. 20
SRI-4	Coal, Sept. 21

SRI-5	Cyclone ash, Sept. 18
SRI-6	Cyclone ash, Sept. 19
SRI-7	Cyclone ash, Sept. 20
SRI-8	Cyclone ash, Sept. 21
SRI-11	ESP ash, Sept. 18
SRI-12	ESP ash, Sept. 20

UNIVERSITY OF MISSOURI-COLUMBIA

Research Reactor Facility

Research Park
Columbia, Missouri 65211
Telephone (314) 882-~~4211~~
FAX (314) 882 – [illegible]
63

March 30, 1992

FAX: 205-581-2726

Edward B. Dismukes
Southern Research Institute
P.O. Box 55305
Birmingham, AL 35255-5305

Dear Ed:

Forgive me for not responding to your letter of March 20 until today. I was attending a meeting in Los Angeles last week. I will be here this week and then gone again most of next week to attend a meeting in Pittsburgh.

I have enclosed the results from our analysis of the second batch of coal and ash specimens using INAA. A second copy will be sent by regular mail.

The glass tube packed with charcoal for collection of mercury vapor is a difficult analytical problem. In particular, the glass tube and copper/aluminum mesh when irradiated will emit a very high signal causing the mercury to be nearly impossible to observe. Thus, the only way I can analyze the sample would be by removing the charcoal and placing it into one of my irradiation vials. I assume the charcoal has not been impregnated with Ag or some other element. The charges would be the same as with other analyses already conducted for you. Please call if you have any questions.

Sincerely,

Michael D. Glascock

Michael D. Glascock

Enclosures

COLUMBIA KANSAS CITY ROLLA ST. LOUIS

an equal opportunity institution

Table I. Concentrations of Major and Trace Elements in Coal and Ash Samples (March 1992).

Ident.	Al (%)	As (ppm)	Ba (ppm)	Ca (%)	Ce (ppm)	Co (ppm)	Cr (ppm)	Cs (ppm)	Dy (ppm)	Eu (ppm)
G449-32-5	1.00	3.4	62	0.12	10	2.6	16	1.0	0.52	0.17
G449-32-6	0.82	3.8	67	0.19	9	2.3	13	0.5	0.83	0.18
G449-32-7	1.09	3.4	59	0.26	10	2.4	17	1.0	0.56	0.17
G449-32-8	0.94	4.0	54	0.29	10	2.4	17	1.0	0.63	0.17
G449-32-9	1.01	3.8	52	0.34	10	2.5	18	1.0	0.53	0.18
G449-32-16	9.26	33.3	463	3.40	102	25.4	162	9.9	6.14	1.67
G449-32-19	9.64	35.5	524	3.47	103	25.3	177	10.1	6.40	1.69
G449-32-22	9.62	41.0	429	3.25	106	25.7	187	10.7	6.31	1.71
G449-32-25	9.82	40.1	481	3.48	105	26.1	186	10.6	6.80	1.75
G449-33-2B	14.45	155.7	1401	1.06	178	46.8	207	11.1	14.68	3.82
G367-54A	9.28	69.2	547	3.33	101	27.1	189	12.2	6.60	1.79
G367-54B	10.18	86.0	607	3.03	106	28.2	212	13.7	6.98	1.82
G367-54C	9.61	64.6	503	3.19	102	24.6	201	12.1	6.86	1.73
G367-54D	9.95	83.3	597	3.45	107	28.8	216	13.2	7.11	1.81

<u>SRMs from National Institute of Science and Technology</u>

G449-32-6	Coal, 1632b
G449-33-2B	Fly ash, 1633a

<u>Samples from Site 110, January 1992</u>

G449-32-5	Coal, Jan. 14	G449-32-16	ESP ash, Jan. 14	G367-54A	Metals train ash, Jan. 14
G449-32-7	Coal, Jan. 15	G449-32-19	ESP ash, Jan. 15	G367-54B	Metals train ash, Jan. 15
G449-32-8	Coal, Jan. 16	G449-32-22	ESP ash, Jan. 16	G367-54C	Metals train ash, Jan. 16
G449-32-9	Coal, Jan. 17	G449-32-25	ESP ash, Jan. 17	G367-54D	Metals train ash, Jan. 17

Table I. Concentrations of Major and Trace Elements in Coal and Ash Samples (March 1992).

Ident.	Fe (%)	Hf (ppm)	Hg (ppb)	K (%)	La (ppm)	Lu (ppm)	Mn (ppm)	Mo (ppm)	Na (%)	Nd (ppm)
G449-32-5	1.2	0.59	< 32	0.24	4.5	0.07	19.7	10.9	0.04	4.5
G449-32-6	0.8	0.47	< 34	< 0.08	4.4	0.05	12.9	2.5	0.05	3.3
G449-32-7	1.3	0.56	< 31	0.24	4.5	0.09	18.2	10.8	0.04	3.1
G449-32-8	1.3	0.55	< 38	0.19	4.5	0.13	18.4	10.2	0.04	3.4
G449-32-9	1.2	0.58	< 29	0.20	4.9	0.10	20.8	10.5	0.05	3.6
G449-32-16	11.8	5.73	< 43	2.03	47.5	0.98	202.0	81.7	0.36	41.0
G449-32-19	13.1	5.96	< 33	2.03	48.6	1.07	196.4	96.1	0.41	49.4
G449-32-22	12.3	6.17	< 41	2.13	49.4	1.08	195.8	109.2	0.42	46.7
G449-32-25	11.9	6.07	< 32	2.05	48.8	1.03	203.8	101.5	0.41	43.9
G449-33-2B	9.8	8.05	< 42	1.95	83.8	1.16	190.5	31.7	0.17	77.6
G367-54A	9.0	5.74	< 35	2.32	46.5	1.06	206.0	124.3	0.44	44.9
G367-54B	9.8	6.19	< 43	2.57	48.7	1.13	196.6	159.3	0.51	44.3
G367-54C	8.5	5.68	< 39	2.17	46.6	1.14	195.5	145.9	0.47	46.9
G367-54D	9.8	5.98	< 36	2.41	48.7	1.13	218.8	166.2	0.47	46.4

SRMs from National Institute of Science and Technology

G449-32-6	Coal, 1632b
G449-33-2B	Fly ash, 1633a

Samples from Site 110, January 1992

G449-32-5	Coal, Jan. 14	G449-32-16	ESP ash, Jan. 14	G367-54A	Metals train ash, Jan. 14
G449-32-7	Coal, Jan. 15	G449-32-19	ESP ash, Jan. 15	G367-54B	Metals train ash, Jan. 15
G449-32-8	Coal, Jan. 16	G449-32-22	ESP ash, Jan. 16	G367-54C	Metals train ash, Jan. 16
G449-32-9	Coal, Jan. 17	G449-32-25	ESP ash, Jan. 17	G367-54D	Metals train ash, Jan. 17

Table I. Concentrations of Major and Trace Elements in Coal and Ash Samples (March 1992).

Ident.	Ni (ppm)	Rb (ppm)	Sb (ppm)	Sc (ppm)	Se (ppm)	Sm (ppm)	Sr (ppm)	Ta (ppm)	Tb (ppm)	Th (ppm)
G449-32-5	< 15	11	1.5	2.2	1.77	1.0	< 24	0.14	0.11	1.5
G449-32-6	< 13	6	0.2	2.1	1.08	0.9	98	0.14	0.10	1.4
G449-32-7	< 16	13	1.5	2.3	0.66	1.0	< 26	0.14	0.17	1.5
G449-32-8	< 15	13	1.6	2.2	2.28	1.0	13	0.14	0.11	1.5
G449-32-9	< 16	16	1.4	2.3	1.67	1.0	< 26	0.17	0.13	1.6
G449-32-16	83	138	14.3	22.8	1.67	9.8	115	1.36	1.08	15.5
G449-32-19	< 64	137	16.3	23.9	1.42	10.2	52	1.36	1.14	16.2
G449-32-22	58	146	18.3	24.5	1.10	10.4	127	1.49	1.14	16.6
G449-32-25	98	145	17.7	24.2	1.97	10.4	131	1.47	1.08	16.2
G449-33-2B	103	140	6.6	40.9	6.51	17.8	848	2.11	2.95	25.6
G367-54A	113	164	26.8	24.6	15.22	10.5	274	1.45	1.03	16.2
G367-54B	81	174	34.9	26.2	11.22	11.2	140	1.63	1.08	17.2
G367-54C	79	157	27.6	24.1	16.79	10.8	218	1.52	1.21	15.8
G367-54D	140	166	33.3	25.5	13.30	11.3	< 108	1.54	1.50	16.5

SRMs from National Institute of Science and Technology

G449-32-6	Coal, 1632b
G449-33-2B	Fly ash, 1633a

Samples from Site 110, January 1992

G449-32-5	Coal, Jan. 14	G449-32-16	ESP ash, Jan. 14	G367-54A	Metals train ash, Jan. 14
G449-32-7	Coal, Jan. 15	G449-32-19	ESP ash, Jan. 15	G367-54B	Metals train ash, Jan. 15
G449-32-8	Coal, Jan. 16	G449-32-22	ESP ash, Jan. 16	G367-54C	Metals train ash, Jan. 16
G449-32-9	Coal, Jan. 17	G449-32-25	ESP ash, Jan. 17	G367-54D	Metals train ash, Jan. 17

Table I. Concentrations of Major and Trace Elements in Coal and Ash Samples (March 1992).

Ident.	Ti(%)	U(ppm)	V(ppm)	Yb(ppm)	Zn(ppm)	Zr(ppm)
G449-32-5	0.04	2.2	79	0.39	28	28
G449-32-6	0.05	0.6	15	0.37	10	< 14
G449-32-7	0.07	2.2	73	0.41	27	32
G449-32-8	0.04	2.7	75	0.38	21	40
G449-32-9	0.08	2.1	83	0.43	23	25
G449-32-16	0.58	21.4	625	4.14	263	281
G449-32-19	0.56	22.2	743	4.45	255	274
G449-32-22	0.64	23.3	784	4.24	301	320
G449-32-25	0.55	25.1	781	4.39	321	310
G449-33-2B	0.83	10.3	298	7.98	241	302
G367-54A	0.55	25.0	780	4.41	424	281
G367-54B	0.63	28.8	956	4.65	478	331
G367-54C	0.62	28.4	979	4.32	426	356
G367-54D	0.58	31.0	988	4.37	534	325

SRMs from National Institute of Science and Technology

G449-32-6	Coal, 1632b
G449-33-2B	Fly ash, 1633a

Samples from Site 110, January 1992

G449-32-5	Coal, Jan. 14	G449-32-16	ESP ash, Jan. 14	G367-54A	Metals train ash, Jan. 14
G449-32-7	Coal, Jan. 15	G449-32-19	ESP ash, Jan. 15	G367-54B	Metals train ash, Jan. 15
G449-32-8	Coal, Jan. 16	G449-32-22	ESP ash, Jan. 16	G367-54C	Metals train ash, Jan. 16
G449-32-9	Coal, Jan. 17	G449-32-25	ESP ash, Jan. 17	G367-54D	Metals train ash, Jan. 17

APPENDIX C

CORRESPONDENCE AND REPORTS
from
Nicolas Bloom
Brooks Rand, Ltd.

MERCURY SPECIATION

Names of the plant (Site 110)
and its location have been
deleted to avoid identification.

BROOKS RAND, LTD.
3960 Sixth Avenue Northwest
Seattle, WA 98107
Phone: (206) 632-6206

October 21, 1991

Ed Dismukes
Southern Research Institute
P.O. Box 55305
Birmingham, Al 53255-5305

Dear Dr. Dismukes,

Enclosed please find my report on mercury speciation at the powerplant, as well as a copy of the invoice, already submitted to accounts payable. Although the total number of samples analysed was one less than anticipated, there were additional costs related to Eric's longer than anticipated stay in I hope that there will be no trouble paying the entire invoice--if so, please let me know.

Overall, I think that the results look good, but lack of concurrent sampling for total Hg, or simultaneous sampling at the hot and cold sides, makes it difficult to verify the accuracy of the results. **If at all possible, could you tell me sometime this week what the expected Hg concentrations were at this site (based upon input coal mercury levels).** It would be great if the EPA-methodology numbers were in too, but I will not hold my breath. In the future, I think that we will collect simultaneous samples for total and speciation, to provide our own internal QA.

I have sent a copy of this report directly to Roy Clarkson (Southern Company), and Don Porcella (EPRI), to help facilitate having my paper for the Air Toxics conference approved. Thank you for your support of my research. I look forward to working with you again in the future.

Sincerely,

Nicolas Bloom

Mercury Speciation in the Stack Gases of the Coal Fired Power Plant (September 18-21, 1991)

Nicolas S Bloom
Brooks Rand, Ltd.
3950 6th Avenue NW
Seattle, WA 98107

October 21, 1991

Sampling. Stack gas samples were collected from both the hot side and the cold side of the ESP at the power plant over the period from September 18-21, 1991. Generally, one sample from each point was collected each day, with a goal of 4 hot side and 4 cold side samples. The hot side and cold side samples were collected at different times each day, so they are not directly comparable. Samples of 40 L volume were collected by vacuum at a flow rate of 0.5 L/min, using a heated (115°C) quartz sampling probe. The probe was designed to sample 1.5 m inside the stack, but it broke off on the first sample, resulting in all samples being collected at about 0.5 m inside the stack.

Samples were collected through a stack of dry sorbants consisting first of two tandem KCl-soda lime traps (to collect oxidized Hg species), and then two tandem iodated carbon traps (to collect Hg^0). The tandem trapping works to allow an assessment of the trapping efficiency for the various species. No filter was used, so that particulate Hg is included as part of the oxidized Hg fraction.

Because Brooks Rand, Ltd. has no isokinetic sampling equipment, particulate samples were collected by SRI, and aliquots shared with Brooks Rand. Originally, our intent was to collect our samples filtered through quartz wool plugs, and to only analyse the gas-phase samples, adding to them, afterwards the data generated from the SRI particulates. Equipment difficulties prohibited our prefiltering the gas-phase samples, however, so that the particulates were collected onto the soda-lime traps. Thus, gas-phase concentrations for Hg(II) and CH_3Hg were determined by subtracting the mean particulate levels determined on the SRI samples from the measured results from the soda lime traps. Although the particulate on the soda-lime traps was not collected isokinetically, and so probably underrepresents the actual particulate contribution, the potential error is small, given the very small fraction of the total Hg represented by the particulates.

Analysis. Elemental Hg was determined as total Hg on the iodated traps in the following way: The entire contents of each trap were emptied into a 18.2 mL teflon vial, and 3 mL of 7:3 HNO_3/H_2SO_4 were added. The vials were sealed, and the contents digested at 70°C for 3

h. The samples were then diluted to 18.2 mL with 0.02N BrCl in 10% HCl. Aliquots of from 25 to 200 µL were reduced with $SnCl_2$, and the Hg^o then purged onto a gold coated sand trap. Analysis was achieved by thermally desorbing the Hg into an argon stream, flowing into a cold vapour atomic fluorescence (CVAFS) detector. The total number of ng Hg in each sample was then calculated from the volume ratio of aliquot to 18.2 mL. The mean of mercury values on the backup traps, which was found to be indistinguishable from new blank iodated carbon traps, was subtracted to give the net ng Hg per sample. Concentration Hg^o was then calculated by dividing this net ng per sample by the sample volume in m^3 (0.040).

The KCl-soda lime traps, including the glasswool plugs, were digested in 125 mL of 10% HCl, in teflon bottles, until all of the soda-lime was dissolved (about 3 hours). This solution was then analysed for Hg(II), by direct $SnCl_2$ reduction, and the steps outlined above. An aliquot of each sample was also in the same way analysed for total Hg, after first oxidizing with BrCl. The total and ionic mercury values were indistinguishable from eachother, indicating that no significant quantity of any species except Hg(II) was collected on these traps. Analysis of first and second traps indicated that the trapping efficiency was 81.2 ± 6.3% per trap, for an overall collection efficiency of 96.5%. The Hg(II) and Hg^o values were not corrected for this small deviation from 100%, as it is within the analytical noise. In the next sampling set, larger soda-lime traps will be employed, to increase sampling efficiency to >95% per trap.

The soda-lime trap solution was also analysed for methylmercury, using methylene chloride extraction, reextraction into pure water, aqueous phase ethylation, cryogenic GC separation of the ethyl analogs, and CVAFS detection. The methylmercury values were very small, making assessment of trapping efficiency very difficult. From the data, however, the efficiency is at least 80% per trap. Alkaline digestates (25% KOH in methanol) of particulate samples collected by SRI were analysed for methylmercury by the same method. All methylmercury results were calibrated by the method of standard additions, to take into account any potential interferences. No differences in standards were observed between sample matricies and deionized water.

Summary of QA/QC results. Listed below is a summary of the important QA/QC results generated in the laboratory. Individual data are available on request. Unfortunately, no provision was made to provide field QA/QC data (simultaneous replicates, *in situ* spikes, etc.), so this data represents only the analytical side of the QA/QC. The sampling efficiency results, are true field data, however, from tandem trapping.

Method Blanks (0.040 m^{-3} sample size)
elemental mercury: 0.021 ± 0.019 $\mu g \cdot m^{-3}$ (n=10)
ionic Hg(II): 0.019 ± 0.002 $\mu g \cdot m^{-3}$ (n=2)
methyl mercury: 0.00053 ± 0.00011 $\mu g \cdot m^{-3}$ (n=3)
particulate total Hg: 0.003 ± 0.000 $\mu g \cdot m^{-3}$ (n=2)
particulate methyl Hg: <0.002 $\mu g \cdot m^{-3}$ (n=2)

Hg^o Sampling efficiency
mean ng Hg/carbon trap (first): 69.34 ± 49.80 (n=7)
(backup trap): 0.28 ± 0.58 (n=7)
mean recovery on first trap (%): 97.9 ± 3.2

Hg(II) Sampling efficiency
mean ng Hg(II)/trap (first): 148.25 ± 54.35 (n=6)
(backup trap): 35.97 ± 20.07 (n=6)
mean recovery on first trap (%): 81.2 ± 6.3

CH_3Hg Sampling Efficiency
mean ng CH_3Hg/trap (first): 0.054 ± 0.030 (n=4)
(backup trap): <0.005 (n=2)
recovery on first trap (%): >81 to >95

CH3Hg Extraction Efficiency
mean efficiency from Na-Lime 85.2 ± 11.1 (n=7)
historical mean from DDW $82. \pm 5.$

Total versus Hg(II) on Soda Lime Traps
% of total as Hg(II), front traps: 100.2 ± 3.1 (n=7)
% of total as Hg(II), backups: 108.6 ± 2.6 (n=5)
[labile($\mu g \cdot m^{-3}$) = 0.96•total($\mu g \cdot m^{-3}$) + 3.8 (n=13, r=0.999)]

Analytical Replicates ($\mu g \cdot m^{-3}$ Hg)
Hgo 9/20/91 cold side: 1.280; 1.233; 1.263
Hgo 9/21/91 cold side 1.153; 1.147; 1.141
Hg(II) all days: *see total vs Hg(II) above*
CH_3Hg 9/20 cold side: 0.0019; 0.0014

Comments. The data look reliable, although it is curious that the mean of results for the hot side are lower than for the cold side. The standard deviations overlap, however, and the sample sizes are too small to read much significance into this. However, in the future, it would be best to monitor the hot side and cold side simultaneously, so that the numbers are directly comparable. The sampling efficiency for the iodated carbon traps was 100%, and though for the soda-lime traps it was 81%, it was quite reproducible between runs. No analytical difficulties (interferences, etc.) were noted for any matrix, with the exception that the large Hg(II) values in the soda-lime trap digestates resulted at first in elevated methylmercury peaks. This was overcome by the methylene chloride extraction, which excludes most of the Hg(II).

Two interesting chemical differences are readily apparent from the data: On the hot side, a greater percentage of Hg is in the elemental form, and CH_3Hg was only detected on the cold side. Both of these observations would be expected, given the thermal stability of oxidized mercury species. Although the values are low, it is somewhat surprising to find any particulate Hg on the hot side samples. Although it is our current belief that the Hg(II) collected on the KCl-soda lime traps is actual ambient Hg(II), this has yet to be proven with careful field spiking experiments. Until this is done, the possibility remains that some fraction of the Hg(II) observed actually represents on-line oxidation of Hg^o. It is hoped that this question will be resolved at the EPRI sponsored Somerset project, in the spring of 1992.

New sampling equipment, made with a stainless steel probe sheath, is being constructed, to minimize breakage in the future. Also, a total of 4 sampling systems will be constructed, to allow simultaneous sampling at two or more points, for QA purposes. For best QA of the data, mercury sampling should be conducted on a separate sampling schedule from the other work at the site, to allow for the use of simultaneous sampling of hot and cold sides, and/or simultaneous sampling of speciation and total Hg.

Site:
Type:**Coal Fired**
Dates:**September 18-21, 1991**

date	location	sample volume (m^3)	mercury concentrations, $\mu g \cdot m^{-3}$ (STP, as Hg)						
				particulate		gas phase			
			total	total	methyl	total[a]	Hg^o	Hg(II)	methyl
9/18/91	cold side	0.040	6.16	n.d.	n.d.	6.16	0.71	5.45	0.0009
9/19/91	cold side	0.040	6.80	n.d.	n.d.	6.80	2.13	4.67	0.0022
9/20/91	cold side	0.040	8.23	n.d.	n.d.	8.23	1.26	6.97	0.0016
9/21/91	cold side	0.017	7.35	n.d.	n.d.	7.35	1.15	6.20	0.0013
9/17/91	hot side	0.040	3.95	n.d.	n.d.	3.83	1.77	2.06	<0.0001
9/18/91	hot side	b	n.d.	0.368	<0.002	n.d.	n.d.	n.d.	n.d.
9/19/91	hot side	b	n.d.	0.108	<0.002	n.d.	n.d.	n.d.	n.d.
9/20/91	hot side	0.040[b]	6.96	0.029	<0.002	6.83	1.47	5.36	<0.0001
9/21/91	hot side	0.040[b]	5.33	0.025	<0.002	5.21	4.24	0.97	<0.0001

[a] Total gas phase for cold side samples is reported as the same as total, because no filters were collected. However, particulate loading on the cold side was trivial, so that this approximation is probably accurate within our ability to measure.

[b] Hot side particulate samples were collected by SRI, using different sampling equipment, 1 gram composites (of the various particle size fractions collected) were then sent to Brooks Rand in teflon vials for analysis. The values for total and Hg(II) gas phase Hg represent the measured values for these fractions, minus the mean particulate mercury (0.132 +/- 0.162 $\mu g/m^3$ (n=4), since particulate samples were not collected at the same time as the speciation samples.

	cold side (n=5)		**hot side (n=3)**	
	mean	S.D.	mean	S.D.
total Hg ($\mu g/m^3$)	7.14	0.87	5.41	1.51
% Hg^o	18.9	8.4	48.4	29.3
% Hg(II)	81.1	8.4	49.1	29.5
% particulate Hg	--	--	2.4	3.0
% methyl Hg	0.021	0.008	<0.002	--

BROOKS RAND, LTD.
3960 Sixth Avenue Northwest
Seattle, WA 98107
Phone: (206) 632-6206

March 18, 1992

Ed Dismukes
Southern Research Institute
P.O. Box 55305
Birmingham, Al 53255-5305

Dear Dr. Dismukes,

Enclosed please find my report on mercury speciation at the powerplant (January, 1992), as well as 2 copies of the invoice. As you will see from the data, we encountered considerable problems this round, especially in relation to the hot-side sampling. Although we have spent considerable effort trying to discover the cause of the low results from the hot side (see discussion in report), we have yet to find an explanation. Thus, we are only billing for the results obtained from the cold side and the hot side particulate data, where available. I am sorry for the poor results from this run--I expect that it is a sampling related problem, hopefully which we will resolve at our upcoming EPRI funded QA projects.

At this point I should also note that I will soon be leaving Brooks Rand, to my own company, Frontier Geosciences. My new company will focus only on publishable research, and thus I will be unavailable for work such as this in the future. However, if you continue to need these analytical services, Brooks Rand, Ltd. will continue in the business of mercury speciation routine analysis. The person to talk with in the interim is Richard Brooks, the owner. I will still remain affiliated with Brooks Rand as an advisor for approximately one year.

Sincerely,

Nicolas Bloom

Mercury Speciation in the Stack Gases of the Coal Fired Power Plant (January 14-17, 1992)

Nicolas S Bloom
Brooks Rand, Ltd.
3950 6th Avenue NW
Seattle, WA 98107

March 18, 1992

Sampling. Stack gas samples were collected from both the hot side and the cold side of the ESP at the power plant over the period from January 14-17, 1992. Generally, one sample from each point was collected each day, with a goal of 4 hot side and 4 cold side samples. The hot side and cold side samples were collected at different times each day, so they are not directly comparable. Samples of 20 L volume were collected by vacuum at a flow rate of 0.35 L/min, using a heated (115°C) quartz sampling probe. The probe was designed to sample 1.0 m inside the stack.

Samples were collected through a stack of dry sorbants consisting first of a quartz wool filter, then two tandem KCl-soda lime traps (to collect oxidized Hg species), and then two tandem iodated carbon traps (to collect Hg^o). The tandem trapping works to allow an assessment of the trapping efficiency for the various species. The filters were analysed for total particulate mercury, although they were not isokinetically collected. Because the mercury on particulates is vanishingly small, the error due to non-isokinetic sampling is insignificant to the mercury budget. Methylmercury was not analysed on the particulates, as it would be well below the limits of detection, given the total Hg levels. Two particulate samples from the hot side were analysed on a mass rather than a volume basis, because it was apparent by inspection that some of the very high particulate loading had fallen out of the filter upon retrieval, making a per volume calculation impossible.

Analysis. Elemental Hg was determined as total Hg on the iodated traps in the following way: The entire contents of each trap were emptied into a 18.2 mL teflon vial, and 3 mL of 7:3 HNO_3/H_2SO_4 were added. The vials were sealed, and the contents digested at 70°C for 3 h. The samples were then diluted to 18.2 mL with 0.02N BrCl in 10% HCl. Aliquots of from 25 to 200 µL were reduced with $SnCl_2$, and the Hg^o then purged onto a gold coated sand trap. Analysis was achieved by thermally desorbing the Hg into an argon stream, flowing into a cold vapour atomic fluorescence (CVAFS) detector. The total number of ng Hg in each sample was then calculated from the volume ratio of aliquot to 18.2 mL. The mean of mercury values on the backup traps, which was found to be indistinguishable from new blank iodated carbon traps, was subtracted to give the net ng Hg per sample. Concentration Hg^o was then calculated by dividing this net ng per sample by the sample volume in m^3 (0.020).

The KCl-soda lime traps, including the glasswool plugs, were digested overnight in 125 mL of 10% H_2SO_4, in teflon bottles. This solution was then analysed for Hg(II), by direct $SnCl_2$ reduction, and the steps outlined above. Analysis of first and second traps indicated that the trapping efficiency was >95% per trap, so that only the first trap data were used. These traps were larger than those used during the first sampling at accounting for the much better collection efficiency this time.

The soda-lime trap solution was also analysed for methylmercury, using distillation purification, aqueous phase ethylation, cryogenic GC separation of the ethyl analogs, and CVAFS detection. The methyl mercury values were very small, making assessment of trapping efficiency difficult. From the data, however, the efficiency is at least 80% per trap. All methylmercury results were calibrated by the method of standard additions, to take into account any potential interferences. No differences in standards were observed between sample matrices and deionized water.

Summary of QA/QC results (cold side data only). Listed below is a summary of the important QA/QC results generated in the laboratory. Individual data are available on request. Unfortunately, little provision was made to provide field QA/QC data (simultaneous replicates, *in situ* spikes, etc.), so this data represents only the analytical side of the QA/QC. The sampling efficiency results, are true field data, however, from tandem trapping. Please note in the table of data the single data point collected in the field for total mercury (iodated carbon only, #20 cold side), which should equal the sum of all species measured using the speciation train.

Method Blanks (0.020 m^{-3} sample size)

elemental mercury:	0.012 ± 0.004 $\mu g \cdot m^{-3}$ (n=8)
ionic Hg(II):	0.012 ± 0.006 $\mu g \cdot m^{-3}$ (n=3)
methyl mercury:	<0.004 $\mu g \cdot m^{-3}$ (n=3)
particulate total Hg:	0.01 ± 0.01 $\mu g \cdot m^{-3}$ (n=2)

Hg^o Sampling efficiency

mean ng Hg/carbon trap (first):	33.87 ± 58.01 (n=6)
(backup trap):	0.18 ± 0.24 (n=6)
mean recovery on first trap (%):	99.2 ± 1.2 (n=6)

Hg(II) Sampling efficiency	
mean ng Hg(II)/trap (first):	98.50 ± 30.01 (n=4)
(backup trap):	6.11 ± 1.23 (n=4)
mean recovery on first trap (%):	93.3 ± 2.0 (n=4)
CH_3Hg Sampling Efficiency	
mean ng CH_3Hg/trap (first):	0.69 ± 0.53 (n=4)
(backup trap):	<0.1 (n=4)
recovery on first trap (%):	>50 to >95
Mercury absorbed in sampling train ($\mu g \cdot m^{-3}$ Hg)	
	<0.015 ng/m^3 (n=4)

Comments. Clearly, a problem occurred this period with the hot side sampling, as little or no Hg was recovered on any of the traps, for all four sampling attempts (data are presented in the table, in italics, for illustrative purposes only). The data from the cold side look similar to, if a bit lower, than last year's data. We had several hypotheses, which we tested in the laboratory, to try to explain the loss of Hg on the hot side, but none was satisfactory. These were as follows:

1. **That the traps became too hot, allowing breakthrough.** We tested this first by checking the breakthrough of the iodated carbon traps up to 230°C (maximum operating temperature of teflon). Even up to this temperature, no breakthrough was observed, even after 18 Hours of sampling. To further check that the traps could not have been even hotter, we measured the temperature in the probe downstream of a very hot (700°C) gas source. Within 10 cm, the gas temperature had dropped to only 80°C. In the case of our sampling probe, the traps were at least 30 cm from the hottest possible stack temperature.

2. **That the mercury was contained on the (very heavy) loading of particulate matter collected only with the hot-side samples.** Analysis of this particulate matter showed virtually no mercury. Adsorption of Hg on flyash at the hotside temperatures would have been a big surprise, in any case.

3. **That the heavy loading of particulate matter on the hot side blocked the flow, thus diminishing the sample volume.** When we tried, in the laboratory, to pull air

through one of the particulate-packed filters, using the field sampling system, we were at best able to obtain 60 mL/min, whereas the field sampling rate target was about 400 mL/min. The data logs, and conversations with sampling personnel, however, indicate that the flow rate did not drop appreciably during sampling.

At this point, we have two remaining hypotheses, which we will test next time we are in the field. The most likely, is that indeed, the system did become clogged by particulate matter. But, owing to the high operating temperatures (virtually at the melting point of teflon), leaks developed around the teflon fittings, or holes melted through them, which allowed air to continue to flow, around the clogged filter. In this case, the explanation for the low Hg would have to be explained by (a) interaction with the steel sheath tubing--as any gas leaks would occur within that tube, or (b), by virtue of the sheath tubing actually being filled with atmospheric air rather than stack gas, due to the negative pressure on the hot side. The other remaining hypothesis is that a combination of elevated temperature in the traps and high SO_2 levels resulted in breakthrough (our laboratory temperature experiments have generally been conducted in an ordinary air medium).

A hint must be found to this problem in the fact that on the first sampling, we obtained reasonable results on the hot side (albeit slightly lower). The only obvious difference that we can find between the two runs is that this time, we used filters on the ends of the tube, bent toward the direction of flow--resulting in much more particulates being collected than when we had the unfiltered tube end perpendicular to the direction of flow. If you are aware of any other differences between the two runs which might explain this problem, we would be very interested in talking about it.

I think that one reasonable suggestion that I would make, however, is that mercury speciation not be attempted in environments greater than 200°C. This is because both of the maximum temperature for teflon, of 230°C, and because geochemically, it makes no sense. That is because the speciation probably changes upon cooling--and it is only the cooled gas which is released to the atmosphere. For mass balance purposes, then, only total Hg need be measured on the hot side, allowing the construction of special glass-only iodated carbon traps, which have no connectors between the sample and the iodated carbon.

Finally, I note that methyl mercury was not analysed on the particulates, given the low level of total Hg found. Methyl mercury would have been below the limits of detection.

Site:
Type: Coal Fired Powerplant
Dates: January 14-17, 1991

date	location	sample volume (m^3)	mercury concentrations, µg·m^{-3} (STP, as Hg)						
			total	particulate		gas phase			
				total	methyl	total	Hgo	Hg(II)	methyl
01/14	#13 cold	0.020	5.77	0.02	n.d.	5.75	0.60	5.10	0.050
01/14	#9 hot b	0.020	*0.26*	<0.003 µg/g	n.d.	*0.26*	*0.086*	*0.17*	*<0.004*
01/14	#14 hot b	0.020	*0.21*	<0.003 µg/g	n.d.	*0.21*	*0.078*	*0.13*	*<0.004*
01/15	#10 cold	0.020	6.18	0.04	n.d.	6.14	0.55	5.59	0.010
01/15	#20 cold	0.032	4.78*	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
01/15	#11 hot a	0.020	*0.44*	n.d.	n.d.	*0.44*	*0.39*	*0.05*	*<0.004*
01/16	#12 cold	0.020	3.44	0.04	n.d.	3.42	0.38	3.15	0.014
01/17	#16 cold	0.032	7.60	<0.001	n.d.	7.60	0.64	6.90	0.064 ±0.011 (n=5)
01/17	#18 hot a	0.020	*<0.03*	n.d.	n.d.	*<0.02*	*<0.008*	*<0.01*	*0.026*
blanks				0.01			0.012 ± 0.004 (n=8)	0.012 ± 0.006 (n=3)	<0.004 (n=3)

*total only on iodated carbon
n.d. = no data
values in italics are incorrect, as discussed in text (for ilustrative purposes only)
Hot-side particulate levels on a mg/g basis, as unquantified recovery of particulate was observed (see text).

APPENDIX D

QUALITY ASSURANCE/QUALITY CONTROL

D.1 METALS ANALYSIS

Each time a set of samples was analyzed a set of calibration standards and a blank were run to establish the linear calibration equation between instrument signal and concentration. All of the elements to be analyzed were present in each of the calibration standards; the relative concentrations of the individual elements were the same in each standard solution, but the calibration range for each element was extended far enough, normally by the use of five standard solutions, to cover the range of concentrations in the samples being analyzed.

A QC check sample, customarily one of the calibration standards, was run in each group of samples to ensure that the instrument remained in calibration while the samples were being analyzed. Periodically, in addition, an EPA certified quality control sample (from Spex Industries, Inc.) was analyzed for an independent check on instrument performance.

Each calibration standard and each sample were run in duplicate. The average of the instrumental responses for duplicates was used for calculating the calibration equation and for calculating the composition of the sample.

For samples available in essentially unlimited quantity, such as ash from the ESP hoppers, analyses were performed on the solutions prepared directly from the samples and on these solutions with added spikes of each element of concern. For the samples from the metals train, which were available in limited supply, spikes could not be added routinely. Instead, these samples were simulated by mixing the acids that are used to digest the samples from the trains and adding to the mixed acids known concentrations of the elements of interest; these simulations of the train samples with spikes were then analyzed.

All relevant blanks were analyzed. These blanks included the reagents used to assemble a sampling train and the reagents used for sample digestion and analysis: filter, acids, peroxide, and permanganate. The blanks also included the components of a blank train for each test series, which were processed analytically by the same procedures as the components of each train actually used for sampling. The contribution of the blank train was negligible with respect to the data obtained for samples from inlet sampling trains but not with respect to the data for samples from outlet sampling trains. Amounts of the elements found at the outlet were reduced by the amounts found in the blank train.

For an independent assessment of the accuracy of the ICP/AAS analyses, Standard Reference Materials 1632b (coal) and 1633a (fly ash) were analyzed. The results of quadruplicate analyses of each are presented in Tables D-1 and D-2. The results of one analysis of each SRM by neutron activation are also shown in these tables.

The use of an internal standard in the ICP analyses is a QC measure normally used at Southern Research, but an internal standard that could be used successfully was never identified before the project was completed. Yttrium is the customary choice, but this element precipitated in the sample media, presumably because of the presence of high fluoride concentrations. Thorium and zirconium were tried as substitutes, but they failed also. Now, it appears that in the future osmium, purchased as the compound $(NH_4)_2OsCl_6$, may be satisfactory.

D.2 ACID GASES

Blank samples of the carbonate/bicarbonate solutions used in the impingers for trapping the acid gases and blank samples of the water used for rinsing the impingers were set aside each day for later analysis in the field. None of these blanks contained measurable amounts of the analytes of concern.

D.3 ALDEHYDES AND KETONES

Blanks of the 2,4-dinitrophenylhydrazine trapping solution and blanks of the water used for rinsing the DNPH impingers were reserved daily in the field for laboratory analysis along with actual samples. Two blank trains also yielded samples for analysis. The DNPH and water blanks were combined in the same proportions as these components of the sample trains and were analyzed to obtain a single result for each analyte. The blank results for both formaldehyde and acetone were significant in comparison with sample results; blank corrections were applied to the latter as described in Section 5.4 3.

Table D-1
Test of Analytical Performance on Coal[a]

Element	Concentration, μg/g		
	NIST value[b]	ICP/AAS result[c]	NAA result
As	3.72	4.13 (12.4%)	3.8
Ba	67.5	53.6 (4.2%)	67
Cd	0.0573	0.041 (7.2%)	--
Co	2.29	1.24 (6.4%)	2.3
Cr	(11)	4.00 (7.0%)	13
Cu	6.28	4.59 (3.7%)	--
Mn	12.4	11.5 (4.0%)	12.9
Mo	(0.9)	0.82 (3.8%)	2.5
Ni	6.10	3.98 (6.5%)	<13
Pb	3.67	3.42 (7.0%)	--
Sb	(0.24)	no result	0.2
Se	1.29	0.28 (25.6%)	1.08
V	(14)	12.6 (3.6%)	15

[a] SRM 1632b
[b] Values in parentheses are advisory, not certified.
[c] Parenthetical percentages express relative standard deviations.

Table D-2
Test of Analytical Performance on Fly Ash[a]

Element	Concentration, μg/g		
	NIST value[b]	ICP/AAS result[c]	NAA result
As	145	137 (13.7%)	155.7
Ba	(1500)	1206 (2.7%)	1401
Be	(12)	9.65 (9.6%)	--
Cd	1.00	0.80 (1.8%)	--
Co	(46)	46.9 (5.7%)	46.8
Cr	196	134 (3.1%)	207
Cu	118	86.9 (6.4%)	--
Hg	0.16	--	<0.042
Mn	179	150 (2.9%)	190.5
Mo	(29)	24.9 (6.5%)	31.7
Ni	127	99.1 (2.8%)	103
Pb	72.4	43.6 (11.8%)	--
Sb	6.8	6.87 (9.3%)	6.6
Se	10.3	6.03 (13.7%)	6.51
V	297	258 (2.2%)	298

[a] SRM 1633a

[b] Values in parentheses are advisory, not certified.

[c] Parenthetical percentages express relative standard deviations.

D.4 VOLATILE ORGANIC COMPOUNDS

The analytical work with the volatile organic compounds included the QA/QC measures that are required or recommended by EPA in the instructions for sampling and analysis (SW-846 Methods 0030, 5040, and 8240). The highlights of the procedures followed are described in this section.

Sampling. So-called field blanks were included among the materials analyzed. Field blanks included portions of the water that was used to dilute condensates collected in the VOST; the volumes of condensates were usually small and volumetric dilution was necessary for quantitation purposes. Field blanks also included Tenax and Tenax/charcoal sorption tubes that were transported to the field and momentarily exchanged with corresponding tubes that had previously been assembled in sampling trains. No sample air or gas was drawn through these blank tubes.

Trip blanks consisted of Tenax and Tenax/charcoal sorption tubes that were shipped from the laboratory to the field and then back to the laboratory in compartments with the other sorption tubes; however, the end caps were never removed from the tubes in the field and were only removed finally in the laboratory just before the trip blanks were analyzed.

No blank trains of the type described in connection with the sampling of semi-volatile organic compounds were assembled; however, the field blanks described above were practically equivalent to tubes in a blank train.

Method 0030 does not require any exposure of the sampling tubes to ambient air except during brief periods when the caps are removed from the blank tubes. Nevertheless, during the low-NO_x test series, fully assembled trains were set up on the sampling platforms at the inlet and outlet ducts, and ambient air was drawn through the sampling train for 10 min. The result for these so-called air blanks are given in Table 37 and have been discussed.

Analysis. The compound 4-bromofluorobenzene (BFB) was used to ensure that the spectrometer used in the GC/MS analysis remained properly tuned. A standard solution of this compound was analyzed each 12-hour period when GC/MS data were acquired. To satisfy the performance criteria in Method 8240, the spectrometer was required to produce mass spectra with the ions of BFB within specified limits as percentages of the total.

Five-point calibration curves for the condensates and three-point calibration curves for the sorption tubes were generated for each of the target compounds and surrogate compounds. The calibration curves satisfied the requirements of Method 8240.

So-called continuing calibration compounds (CCCs) were used in a standard solution each 12-hour period of GC/MS analysis to ensure that the spectrometer remained properly calibrated for quantitative analysis. The results were consistent with the requirements of Method 8240.

Recoveries of surrogates (the compounds added to condensates or absorption tubes just prior to desorption) are listed below for the first test series, along with acceptable limits from Method 8240:

Compound	Media	Observed limits, %	Required limits, %
1,2-dichloro-ethane-d_4	condensate	90-121	76-114
	Tenax/charcoal	87-125	50-150
toluene-d_8	condensates	88-111	88-110
	Tenax/charcoal	62-162	50-150
4-bromofluobenzene	condensate	77-102	86-115

Most of the recoveries were within the accepted limits, but there were exceptions. Not indicated here are exceptions — usually recoveries below 50% for DCE — that were due to interference from benzene in the samples. BFB was not used as a surrogate with the sorption tubes because of unusually erratic recoveries.

D.5 SEMI-VOLATILE ORGANIC COMPOUNDS

The analytical work with the semi-volatile organic compounds included the QA/QC measures that are required or recommended by EPA in the instructions for sampling and analysis

(SW-846 Methods 0010 and 8270). The highlights of the procedures followed are described in this section.

Sampling. So-called field blanks and blank trains were included in the materials analyzed. Field blanks included portions of the methyl alcohol/ methylene chloride solvent used in the field for rinsing probe, filter compartment, and impingers of the sampling train. Field blanks also included XAD cartridges that were transported to and from the field along with cartridges used in the actual sampling. Blank trains were sampling elements of the MM5 train, which were assembled in the field as was a train to be used for sampling; the blank trains, however, had no air or gas drawn through them. Neither field blanks not blank trains produced analytical results that would have compromised the integrity of field samples.

The XAD resin was cleaned in the laboratory according to Method 0010 specifications prior to being used in the field, as was all of the glassware to be used in the field.

All XAD used in the field or used for blanks was spiked initially in the laboratory with two compounds: 2,4-dichlorophenol-d_3 and 1,2,3-trichloro-benzene-d_3. The quantity of the former was about 100 μg; that of the latter was about 200 μg. These quantities were the same as actual analytes at concentrations of 50 or 100 $\mu g/Nm^3$ for the minimum sampling volume of 2 Nm^3. In actual samples, DCP was recovered at levels of 38-74% of the spike levels in the baseline testing or 88-199% in the low-NO_x testing. TCP was recovered at levels of 100-137% in the first test series and 70-191% in the second. These recoveries were acceptable in terms of the criteria of Method 8270.

Analysis. The compound decafluorotriphenylphosphine (DFTPP) was used to ensure that the spectrometer used in the GC/MS analysis remained properly tuned. A standard solution of this compound was analyzed each 12-hour period when GC/MS data were acquired. To satisfy the performance criteria in Method 8270, the spectrometer produced mass spectra with the ions of DFTPP within specified limits as percentages of the total.

Five-point calibration curves were generated for each of the 68 target compounds, 6 surrogates, and 2 spiking compounds. The calibration curves satisfied the requirements of Method 8270.

So-called continuing calibration compounds (CCCs) were used in a standard solution each 12-hour period of GC/MS analysis to ensure that the spectrometer was properly calibrated for quantitative analysis. The results were consistent with the requirements of Method 8270.

Recoveries of surrogates (the compounds added to the XAD just prior to extraction) are listed below for the first test series, along with acceptable limits from Method 8270:

Compound	Observed limits, %	Required limits, %
2-Fluorophenol	57.0-83.0	21-100
Phenol-d_5	42.0-68.5	10-94
Nitrobenzene-d_5	30.2-56.2	35-114
2-Fluorobiphenyl	45.4-70.6	43-116
2,4,6-tribromophenol	23.4-80.5	10-123
p-Terphenyl-d_{14}	48.8-66.9	33-141

Only one result was outside the acceptable range. Data of similar but somewhat inferior quality were obtained during the second test series (low-NO_x). The filter blank had low recoveries of the early-eluting surrogates. One inlet sample had a high recovery of nitrobenzene-d_5 and one outlet sample had a low recovery of phenol-d_5.

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