7

COMPARISON OF VAPOR AND PARTICULATE COMPOSITION

Most of the substances measured at Plant Yates are distributed between the flue gas (vapor) and particulate matter (bottom ash, collected ESP ash, ash removed in the FGD system, or emitted ash which exits with the flue gas through the stack). Of the organic compounds tested, the semivolatile compounds should be associated with the particulate matter, and the volatile compounds should remain in the vapor phase. (Some of the organic compounds are at least slightly soluble in water and thus may be removed from the flue gas in the wet FGD system.) The sampling and analytical techniques used in the project did not quantify the distribution of the organic compounds between the particulate and vapor phases.

EPA Proposed Method 29 was the primary method used for collecting the trace metals samples at Plant Yates. The anions train used to measure acid gas concentrations is similar to Method 29 in many respects since both are modifications to the Method 5 sampling procedure. In these methods, the particulate and vapor concentrations are analyzed and may be reported separately. However, because of the low vapor-phase concentrations and the high potential for contamination during sampling, sample handling, or analysis, the partitions between particulate and vapor phases should be used cautiously.

Most of the inorganic elements present in the flue gas downstream of the air heater should be in the particulate phase. As is discussed in Section 8, some of the metals will be enriched in the finer particulate sizes, but the vapor pressure of most elements and their compounds is too low for measurable concentrations to be expected in the vapor phase at temperatures of 300°F and below. Exceptions to this include mercury, hydrochloric acid, hydrofluoric acid, and selenium which may have significant vapor concentrations. Selenium may be present either as vaporous compounds such as SeO_2 or as a component enriched in the finer particulate matter.

Tables 7-1, 7-2, and 7-3 show the particulate and vapor-phase distribution of the inorganic substances of interest measured at Yates in the ESP inlet, ESP outlet, and stack streams, respectively. Rather than summing the components of the sampling train, the concentrations of the particulate and vapor phases have been computed and averaged separately. For values reported from the laboratory as below the detection limit, one-half the detection limit was included in the averaging procedure. The average determined in this manner was used to calculate the particulate percentage, even if the average was less than the average detection limit of the non-detected samples. In this event, the average detection limit has also been included in the tables as a less than value in parentheses (<DL). The percentage of the particulate- and vapor-phase concentrations that result from averaging values below detection limits are included in the tables.

Table 7-1
Vapor and Particulate-Phase Distribution at ESP Inlet

Element	Part. Conc. $\mu g/Nm^3$	% Part. DL[a]	Vapor Conc. $\mu g/Nm^3$ [b]		% Vapor DL[c]	% of Element in Particulate Phase
Antimony	33	0%	0.56		0%	98.3%
Arsenic	400	0%	0.083	(<0.17)	100%	100.0%
Barium	4,400	0%	1.5		0%	100.0%
Beryllium	93	0%	0.06		0%	99.9%
Boron	4,200[d]	0%	6,390		0%	39.7%
Cadmium	24	0%	0.11		16%	99.6%
Chloride	6,100	0%	112,000		0%	5.2%
Chromium	2,900	0%	11		0%	99.6%
Cobalt	275	0%	0.34	(<0.74)	55%	99.9%
Copper	770	0%	1.1		0%	99.9%
Fluoride	1.3	0%	8,300		0%	0.0%
Lead	710	0%	0.103	(<0.21)	100%	100.0%
Manganese	2,120	0%	0.051	(<0.10)	100%	100.0%
Mercury	1.3[e]	0%	5.5		0%	19.2%
Molybdenum	320	0%	0.66	(<1.4)	52%	99.8%
Nickel	2,000	0%	7		7%	99.6%
Phosphorus	2,100	0%	7.8	(<16)	100%	99.6%
Selenium	133	0%	0.11	(<0.22)	100%	99.9%
Strontium	2,910	0%	2		0%	99.9%
Vanadium	2,760	0%	1.20		0%	100.0%

Note: The Hg concentration in the sluiced ash has been substituted for the ESP inlet ash Hg concentration since the latter is believed to be biased high.

[a] Percentage of the particulate concentration that results from using measurements below detection limits.

[b] Note: Run 2 has been excluded from the vapor-phase average because of contamination.

[c] Percentage of the vapor concentration that results from using measurements below detection limits.

[d] Boron concentrations from the sluiced fly ash have been substituted for the gas stream particulate concentrations. Chemicals containing boron are used in the digestion procedure used for the gas stream particulate samples.

[e] The sluiced fly ash mercury concentration was substituted for the mercury concentration measured in the ESP inlet particulate. Material balances around the boiler, ESP, and overall plant support the hypothesis that the ESP inlet particulate mercury concentration is biased high.

Table 7-2
Vapor and Particulate-Phase Distribution at ESP Outlet

Element	Part. Conc. μg/Nm^3	% Part. DL[a]	Vapor Conc. μg/Nm^3		% Vapor ND[b]	% of Element in Particulate Phase
Antimony	0.39	0%	0.021		0%	94.8%
Arsenic	16	0%	0.091	(<0.18)	100%	99.4%
Barium	74	0%	1.0		0%	98.7%
Beryllium	1.7	0%	0.093	(<0.16)	57%	94.9%
Cadmium	1.1	0%	0.10		20%	91.1%
Chloride	45	0%	136,000		0%	0.0%
Chromium	23	0%	0.57	(<0.73)	42%	97.6%
Cobalt	4.5	0%	0.54	(<1.0)	31%	89.2%
Copper	16	0%	1.1		16%	93.9%
Fluoride	0.12	0%	7,900		0%	0.0%
Lead	18	0%	0.37		20%	98.0%
Manganese	34	0%	0.055	(<0.11)	100%	99.8%
Mercury	0.126	0%	5.6		0%	2.2%
Molybdenum	8.1	0%	0.61	(<1.4)	37%	93.0%
Nickel	22	0%	1.54	(<2.9)	59%	93.6%
Phosphorus	100	0%	8.49	(<17)	100%	92.2%
Selenium	82	0%	0.12	(<0.23)	100%	99.9%
Strontium	43	0%	1.4		0%	96.9%
Vanadium	54	0%	1		12%	98.2%

[a] Percentage of the particulate concentration that results from using measurements below detection limits.

[b] Percentage of the vapor concentration that results from using measurements below detection limits.

Table 7-3
Vapor and Particulate-Phase Distribution at Stack

Element	Part. Conc. $\mu g/Nm^3$	% Part. DL[a]	Vapor Conc. $\mu g/Nm^3$	% Vapor DL[b]	% of Element in Particulate Phase
Antimony	0.052	0%	0.012	0%	80.6%
Arsenic	1.1	0%	0.089 (<0.18)	100%	92.5%
Barium	2.8	0%	0.082 (<0.14)	54%	97.2%
Beryllium	0.041	0%	0.061 (<0.17)	82%	40.1%
Cadmium	0.59	0%	0.032 (<0.064)	100%	94.9%
Chloride	214	0%	540	0%	28.4%
Chromium	5.1	0%	0.34 (<0.67)	100%	93.8%
Cobalt	0.25 (<0.6)	59%	0.39	0%	39.3%
Copper	0.77	0%	1.2	14%	38.2%
Fluoride	0.051	0%	124	0%	0.0%
Lead	0.50	0%	0.11 (<0.22)	100%	82.1%
Manganese	7.2	0%	0.054 (<0.11)	100%	99.3%
Mercury	0.0071	18%	3.0	0%	0.2%
Molybdenum	1.4	0%	0.12	0%	92.3%
Nickel	39	0%	1.8 (<2.6)	46%	95.7%
Phosphorus	1.3 (<2.6)	100%	8.2 (<16)	100%	13.6%
Selenium	26	0%	0.8	0%	97.1%
Strontium	1.5	0%	0.022 (<0.045)	100%	98.5%
Vanadium	1.6	0%	0.55	0%	74.5%

[a] Percentage of the particulate concentration that results from using measurements below detection limits.

[b] Percentage of the vapor concentration that results from using measurements below detection limits.

At ESP inlet conditions, more than 99% of the mass of the substances of interest were found in the particulate phase. Exceptions to this are chloride, fluoride, and mercury. Most chloride and fluoride exiting the boiler are in the acid gas form (HCl and HF.) In fact, Title III of the Clean Air Act Amendments of 1990, only lists HCl and HF and not chloride and fluoride salts which would be in the particulate form. However, the particulate measurements are included in this section for completeness.

With the exception of mercury, chloride, and fluoride, the particulate phase contains most of the mass of elements at the ESP outlet and stack as well. The percentage found in the particulate phase decreases for some elements in the stack, primarily because the particulate loading (and therefore the particulate concentration of an element on a gas-phase basis) decreases. The gas-phase concentrations of most elements are reasonably consistent at each of the sampling locations. However, these concentrations, while very low, are above those expected. Since the concentrations of the elements in the liquid impinger samples are extremely low (10 ppb level or below for most), contamination of the impinger solutions is the suspected cause.

Field blank concentrations support the hypothesis that contamination may be the cause of the higher-than-expected vapor-phase concentrations of the elements of interest. Table 7-4 compares the stack vapor measurements to the stack field blank concentrations (calculated on an average stack gas volume basis). For most of the elements, the field blank concentration equals or exceeds the measured stack concentration. Since the reagent blanks are generally much lower than the field blanks, sample handling under field conditions is the expected cause of contamination. Possible sources of contamination include incomplete rinsing of the sampling train glassware or inadvertent contact of the rinse solution with external glassware surfaces. Again, because the concentration of these elements is in the ppb range, very little material is required to cause these levels of contamination.

Mercury and fluoride are almost entirely in the vapor phase at the ESP outlet and stack. Chloride shows a substantial particulate percentage at the stack. This high level of particulate chloride is believed to be caused by a minor amount of absorber liquid being re-entrained from the mist eliminator surfaces. Again, this chloride is a calcium salt which is not included on the list of elements and compounds in Title III of the Clean Air Act Amendments of 1990.

Finally, the selenium distribution at Plant Yates is worthy of note. Essentially all of the selenium was found in the particulate phase at Yates, while at most other coal-fired electric utility plants a significant fraction of the selenium has been measured in the vapor phase. (Variability in the selenium data is also high in most cases.) Although the particulate phase contains the selenium, particulate-phase selenium removal efficiency was only 40% (see Table 8-2) compared to greater than 98% removal efficiency for the total particulate matter. All other particulate-phase metals are removed at greater than 90% efficiency. These data indicate that selenium may be reacting or condensing on the particulate filter during gas-phase sampling resulting in a lower-than-expected vaporous selenium concentration. Also note that the spike recovery for the selenium vapor was low, indicating a possible low bias in the vapor-phase selenium concentration.

Table 7-4
Stack Field Blank Versus Vapor Concentration

Element	Vapor Conc. $\mu g/Nm^3$		Field Blank $\mu g/Nm^3$
Antimony	0.012		1.78
Arsenic	0.089	(<0.18)[a]	<0.177
Barium	0.082	(<0.14)	0.734
Beryllium	0.061	(<0.17)	<0.150
Cadmium	0.032	(<0.064)	0.054
Chromium	0.34	(<0.67)	3.19
Cobalt	0.39		1.01
Copper	1.2		1.66
Lead	0.11	(<0.22)	1.08
Manganese	0.054	(<0.11)	10.6
Molybdenum	0.12		0.073
Nickel	1.8	(<2.6)	3.59
Phosphorus	8.2	(<16)	<16.5
Selenium	0.8		<0.228
Strontium	0.022	(<0.045)	0.513
Vanadium	0.55		0.821

[a] The "<" symbol indicates the average D.L. for these substances.

In Table 7-1, the mercury concentration in the sluiced fly ash has been substituted for the mercury concentration measured in the ESP inlet particulate matter because the ESP value is believed to be biased high. (The ESP inlet ash mercury concentration is significantly higher than that measured at most other coal-fired electric utility plants.) As shown in Table 6-2, material balances for mercury around the boiler (205%) and ESP (55%) indicate that the mercury particulate concentration may be high. The overall balance for mercury (101%) is good. (This balance does not use the ESP inlet data.) Since the ESP sluiced ash includes most of the ash at the ESP inlet, concentrations in this stream should be reasonable estimates for the ESP inlet ash concentrations. When this substitution is made, the mercury balances around the boiler (110%) and ESP (102%) become more reasonable.

8

DISTRIBUTION OF HAPs AS A FUNCTION OF PARTICLE SIZE IN THE FLUE GAS AND THE PARTICLE SIZE DISTRIBUTION IN THE ESP

Understanding the distribution of trace metals according to particle size is important in understanding and predicting trace metals emissions rates and removal efficiencies across control devices. For example, if an element was enriched (higher concentration than in the bulk ash) in the fine particulate matter, the removal efficiency for that element across an ESP would be expected to be less than that of the bulk particulate matter. (Theoretically, an ESP does not control the fines as well as the larger particle size fractions.)

Prior to the presentation of results from Plant Yates, expected results based on historical data will be discussed. Trace metals in coal can be grouped into three general categories:

- Elements (and compounds) that are not vaporized during the combustion process and, therefore, are assumed to be uniformly distributed in the bottom ash and fly ash. Included in this category are barium, beryllium, manganese, strontium, vanadium, and, sometimes, chromium and nickel.

- Elements that are partially or completely vaporized in the furnace and then condense as the flue gas temperature drops in cooler regions of the boiler and in downstream equipment. This condensation can occur on the surface of ash particles or by homogenous nucleation, so elements in this category tend to be enriched in the finer fly ash particles. Included here are arsenic, cadmium, copper, lead, molybdenum, and, sometimes, chromium, nickel, and selenium. Antimony and phosphorus may also fall in this category, but not much supporting data on these elements are available as yet.

- Elements that are vaporized and remain primarily in the vapor phase at flue gas temperatures in the stack. Mercury and sometimes selenium fall into this category. Selenium may be present either as vaporous compounds, such as SeO_2, or as a component enriched in the finer particulate matter.

Collection and Analytical Methods

The mass particle size distributions around the ESP can be used to characterize its performance. The size distributions were determined by Anderson High Capacity Source Sampler (4 cuts) for the ESP inlet, by Microtracs laser diffraction for the ESP Field 1 hopper catch and the ESP Field 2 hopper catch, and by University of Washington Mark V cascade impactor (11 cuts) at the ESP outlet.

To convert the size distributions from aerodynamic diameter to physical diameter, it is necessary to know the density of the particles. Particle density measurements were made on samples from the ESP from Plant Yates ESP Hoppers 1-4 on 6/23/93. A helium pycnometer was used to measure the porosity and volume of the ash samples. The samples were then weighed to determine the particle density. The average of three measurements was 2.41 g/cm^3, and it was assumed that this density was representative for all sizes of particles. This value for density was then used in the impactor data reduction to calculate the physical diameters.

Particle Size Distribution and Fractional Efficiency

Figures 8-1, 8-2, 8-3, and 8-4 show the cumulative and differential particle size distribution measured at the inlet and outlet of the ESP. Specific run data for the ESP inlet and outlet PSD tests are included in Appendix C.

The inertial sampling equipment used for these tests is described in Section 5. Sampling was conducted at a fixed, isokinetic flow rate to yield a constant stage cutpoint. The sampling train utilized is essentially a standard EPA reference Method 17 configuration. Stage cutpoints for the cascade impactors and cyclone samplers are derived from empirical calibrations based on operating flow rates, run conditions, and sampler geometry.

ESP particle size data are presented on a physical basis, rather than aerodynamic, using a measured ash density of 2.4 gm/cm^3. The ESP inlet particle size distribution is a direct average of triplicate runs at the same cyclone stage cutpoints. The top and bottom end of the distribution are assumed to be 50 μm and 0.1 μm, respectively. This range was selected to cover the extent of particles which are typical of coal-fired boilers. Mass median diameter and geometric standard deviation of the distribution were estimated graphically, based on the 50 μm upper size limit, assuming a log-normal distribution. The resulting inlet distribution had a mass median diameter of 13 μm with a standard deviation of 4.1 This represents a rather wide spread for an inlet size distribution. Since only four data points are available from the cyclones, it is difficult to discern any more details on the inlet distribution. However, the amount of space charge suppression that was observed in the first field of the ESP does indicate large concentrations of fine particles which would also reflect a large standard deviation.

Data reduction for the outlet PSD follows a standard cascade impactor D_{50} calculation method.[1] Outlet particle size was also extrapolated to a 50 μm upper endpoint. Mass fraction and differential distribution were directly averaged from the raw impactor run data, since stage D_{50} cutpoints were nearly identical between runs. The resulting distribution had a mass median diameter of 4.1 μm and a standard deviation of 3.1. This size is representative of the size distribution commonly measured at the outlet of an ESP.

In Figures 8-3 and 8-4, and Table 8-1, the differential mass has been normalized to the level of the Method 5/29 average measured particulate concentration. This corrects for sample fallout and loss in the particle sizing cyclones and cascade impactor. It also accounts for

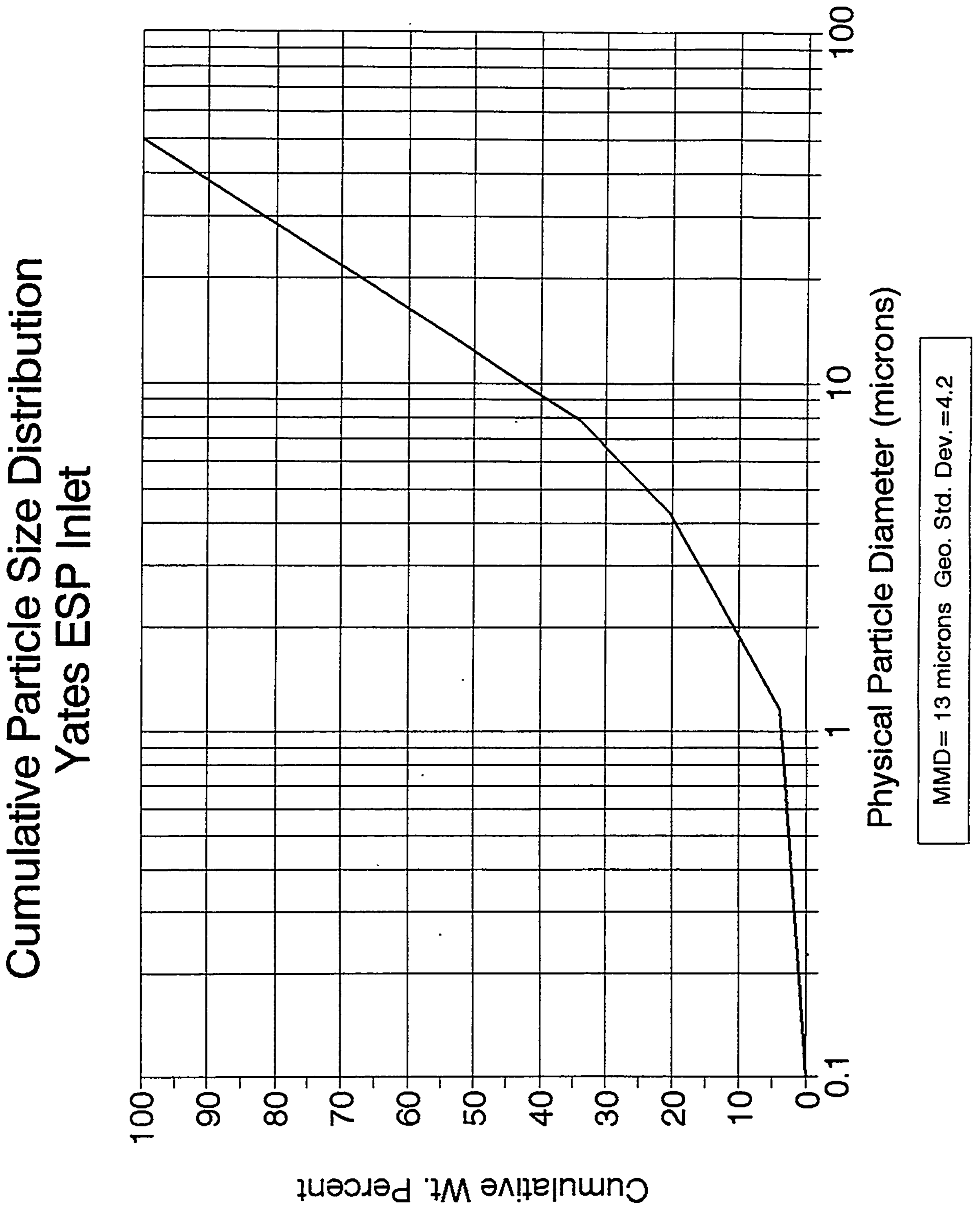

Figure 8-1
Cumulative Particle Size Distribution, Yates ESP Inlet

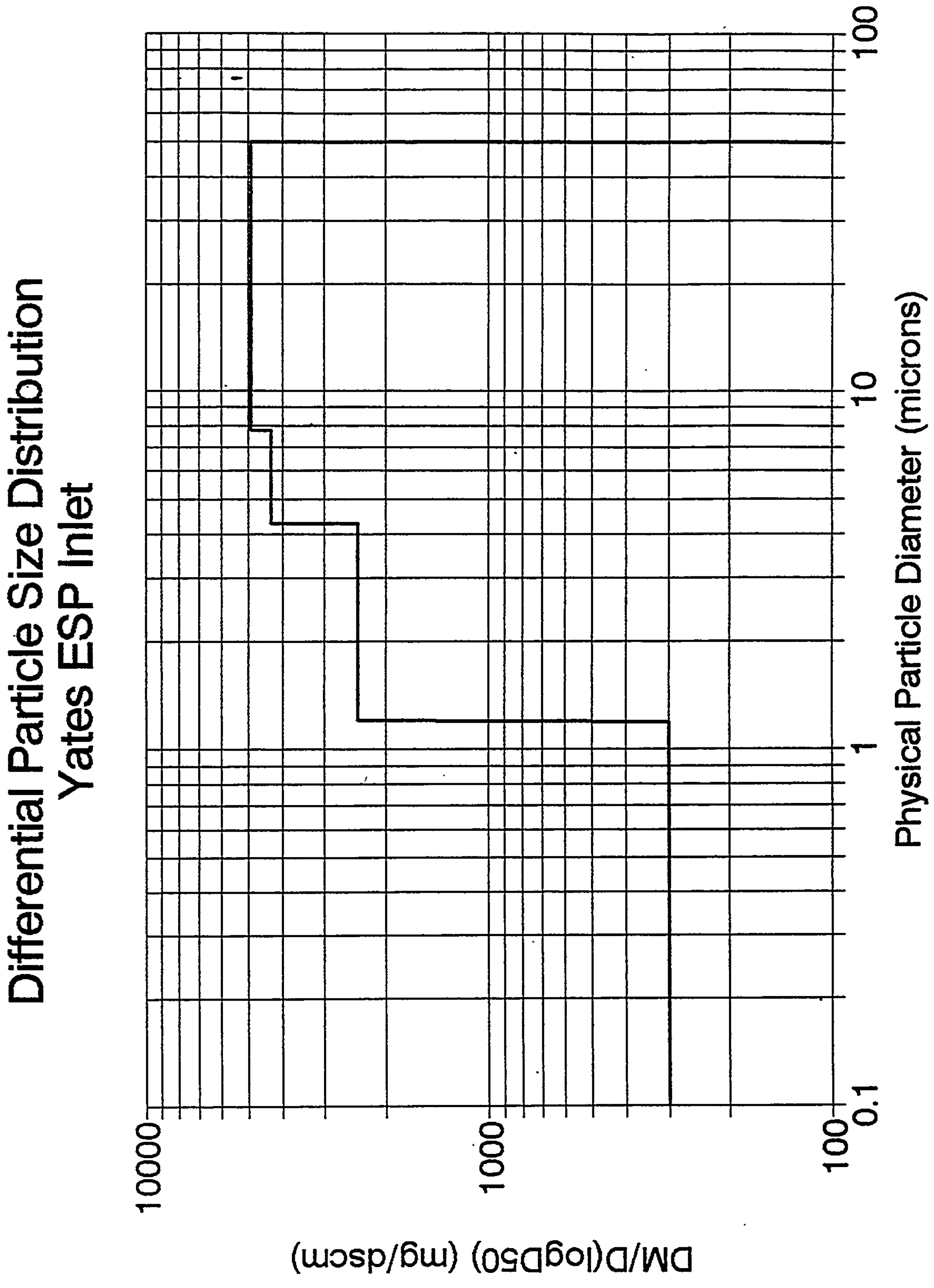

Figure 8-2
Differential Particle Size Distribution, Yates ESP Inlet

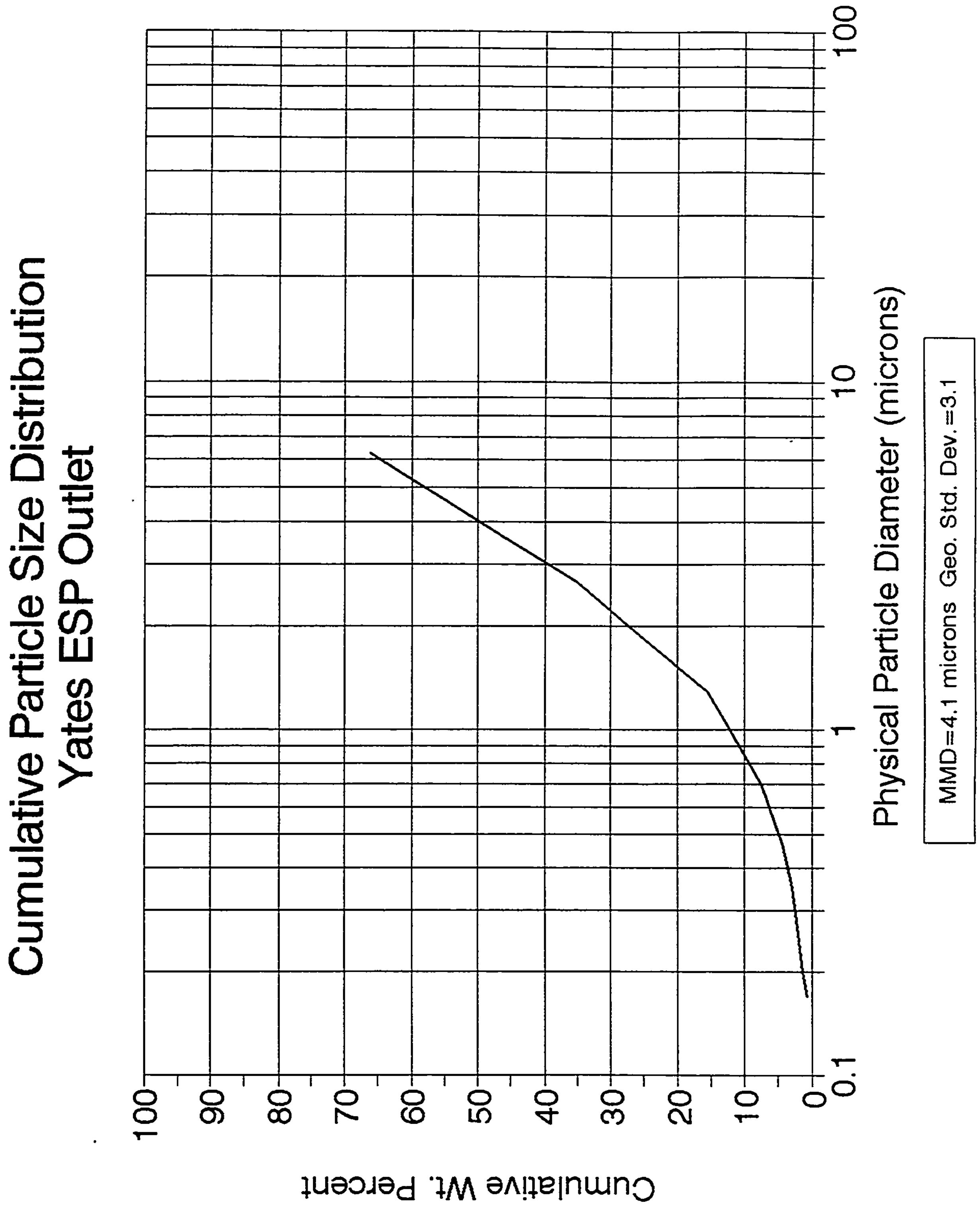

Figure 8-3
Cumulative Particle Size Distribution, Yates ESP Outlet

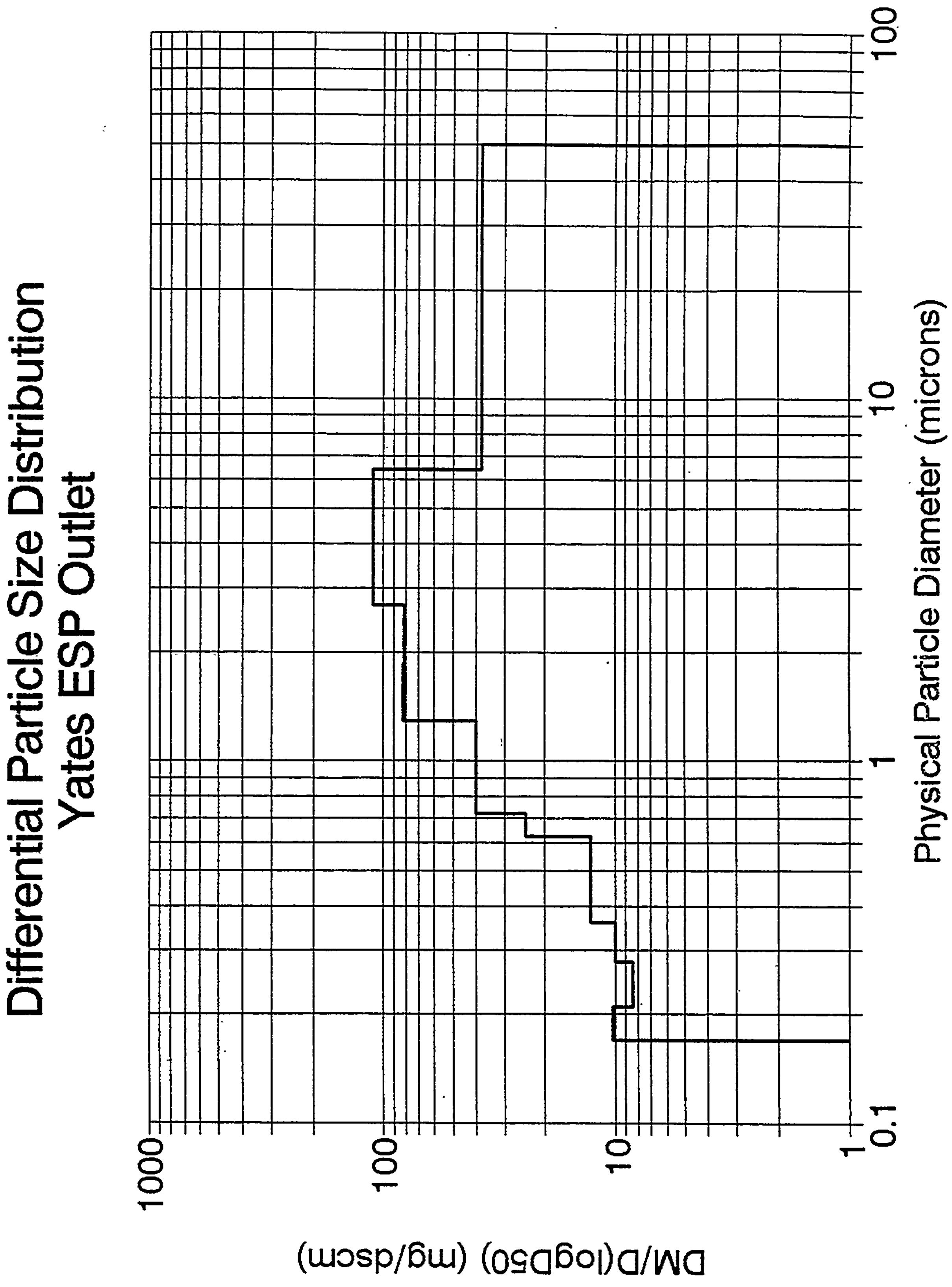

Figure 8-4
Outlet Differential Particle Size Distribution

Table 8-1
Measured Particle Size and Fractional Efficiency

Physical Diameter (microns)	Inlet Cumulative Mass (%)	Inlet DM/d (logD50) (mg/dscm)	Outlet Cumulative Mass (%)	Outlet DM/d(logD50) (mg/dscm)	Fractional Efficiency (%)	Fractional Penetration (%)
0.1 - 1.2	3.8	300	16.0	17.3	94.2	5.8
1.2 - 4.3	20.3	2,413	55.0	81.5	96.6	3.4
4.3 - 7.8	33.8	4,309	78.0	95.5	97.8	2.2
>7.8	100.0	4,927	100.0	51.0	99.0	1.0

Notes:

1. Fly ash density = 2.41 gm/cm^3.
2. Inlet differential distribution normalized to average mass test concentration of 8,338 mg/dscm.
3. Outlet differential distribution normalized to average mass test concentration of 131.8 mg/dscm.

differences between the single-point impactor and cyclone sampler tests and the multipoint Method 5/29 measurements.

Table 8-1 shows the collection efficiency as a function of physical particle size. The overall collection efficiency for all particles was 98.4 percent. The measured collection efficiency for particles below 1.2 μm was 94%, while the collection efficiency for particles between 1.2 - 4.3 microns was 96 percent. The mass fraction above 1 μm represents the majority of particles emitted from the ESP. Although theoretical collection efficiency decreases with the particle diameter, non-ideal effects such as sneakage, gas flow distribution, and reentrainment can have a very significant effect on ESP performance for larger particle sizes. This demonstrates that an ESP can efficiently collect submicron particles and does not emit just fine particles as is commonly believed.

Predicted ESP Performance

ESP performance can be affected by several variables including particle resistivity and the electrical characteristics of the ESP. Both of these conditions can ultimately affect opacity. Each of these are discussed in the following section.

Particle Resistivity. Particle resistivity was measured at the ESP inlet using an extractive resistivity measuring device. In this device, sample collection and resistivity measurement are performed in a chamber external to the duct. The system uses an in-situ probe to isokinetically extract a sample of dust to a temperature-controlled precipitation chamber where a point-plane precipitator deposits the dust onto a disc. Once a suitable layer has been deposited, layer thickness is measured with a precision micrometer. Resistivity is measured in the presence of flue gas by applying increasing voltage across the dust layer. The resulting current is measured with a picoammeter until the dust layer breaks down electrically and sparkover occurs. The resistivity is then calculated using the ratio of the electric field to the current density just prior to sparkover, as described in ASME Power Test Code Number 28. Measurements are typically made over a range of temperatures for the same dust layer. This allows resistivity to be measured over a range of possible ESP operating conditions.

In addition to the in-situ measurements, resistivity was also calculated using a computer model developed by Bickelhaupt.[2,3] This model predicts resistivity as a function of temperature, water vapor content, and SO_3 concentration. An as-received ultimate coal analysis is required to run the Bickelhaupt model.

Figure 8-5 shows a plot of the particle resistivity. The solid triangles are in-situ measurements made during the field test program at the ESP inlet. Although the ESP temperature was steady at approximately 280°F, it was possible to make measurements at a range of temperatures from 240°F to 320°F by varying the temperature in the resistivity chamber.

The lines shown in Figure 8-5 are the predicted values based upon the Bickelhaupt empirical model. This model uses coal and ash characteristics to predict particle resistivity. It has been documented that the weakest part of the model is predicting the gas-phase SO_3 concentration. Therefore, the plot contains the predictions for four values of SO_3 from 0-7 ppm.

At 280°F, the measured resistivity was 8 - 10 x 10^{10} ohm-cm, which represents conditions for very good precipitation. The measured values are higher than the predicted values with greater than 1 ppm of SO_3. The predicted values with no SO_3 match well with the measured values. This means that the amount of SO_3 present in the flue gas was much lower than predicted. This can be caused by conditions in the boiler or by characteristics of the air preheater. Often SO_3 can be scrubbed by the cold surfaces in the heat exchanger.

Another indication that the SO_3 was low was the low dew point that was measured. The resistivity chamber has been modified to allow measurement of acid dew point. A window on the chamber is cooled to a point that condensation occurs on the window face exposed to the flue gas. The window is then heated externally until the mist disappears. A thermocouple attached to the inside of the window is used to determine the temperature of the glass surface. Experience with this system has shown that the dew point can be consistently measured ± 2°F. During the measurements at Plant Yates, there was no detectable dew point above 220°F. This corresponds to an SO_3 concentration of approximately 0.3 ppm.

Electrical Characteristics. The electrical characteristics are shown in Figure 8-6. The voltage current (VI) characteristics are expressed in the normalized terms of electric field strength (kV/cm) and current density (nA/cm^2). All the fields, except Field C, operate at field strengths greater than 3 kV/cm. Cold-side ESPs that are not experiencing problems related to high resistivity will typically operate in the range of 3.0 to 3.5 kV/cm. Therefore, the VI curves shown in Figure 8-6 reflect the moderate particle resistivity levels described previously.

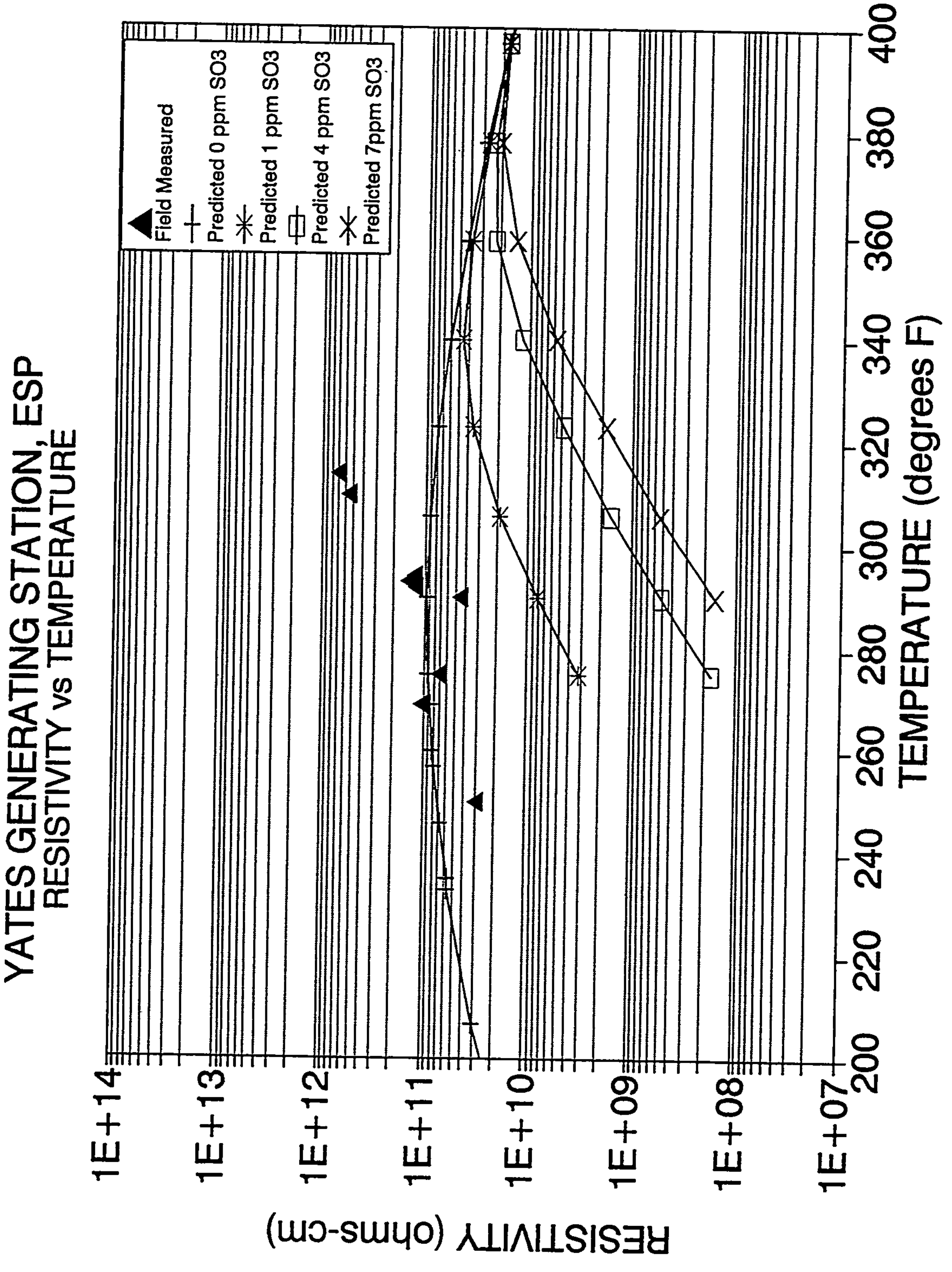

Figure 8-5
Particle Resistivity

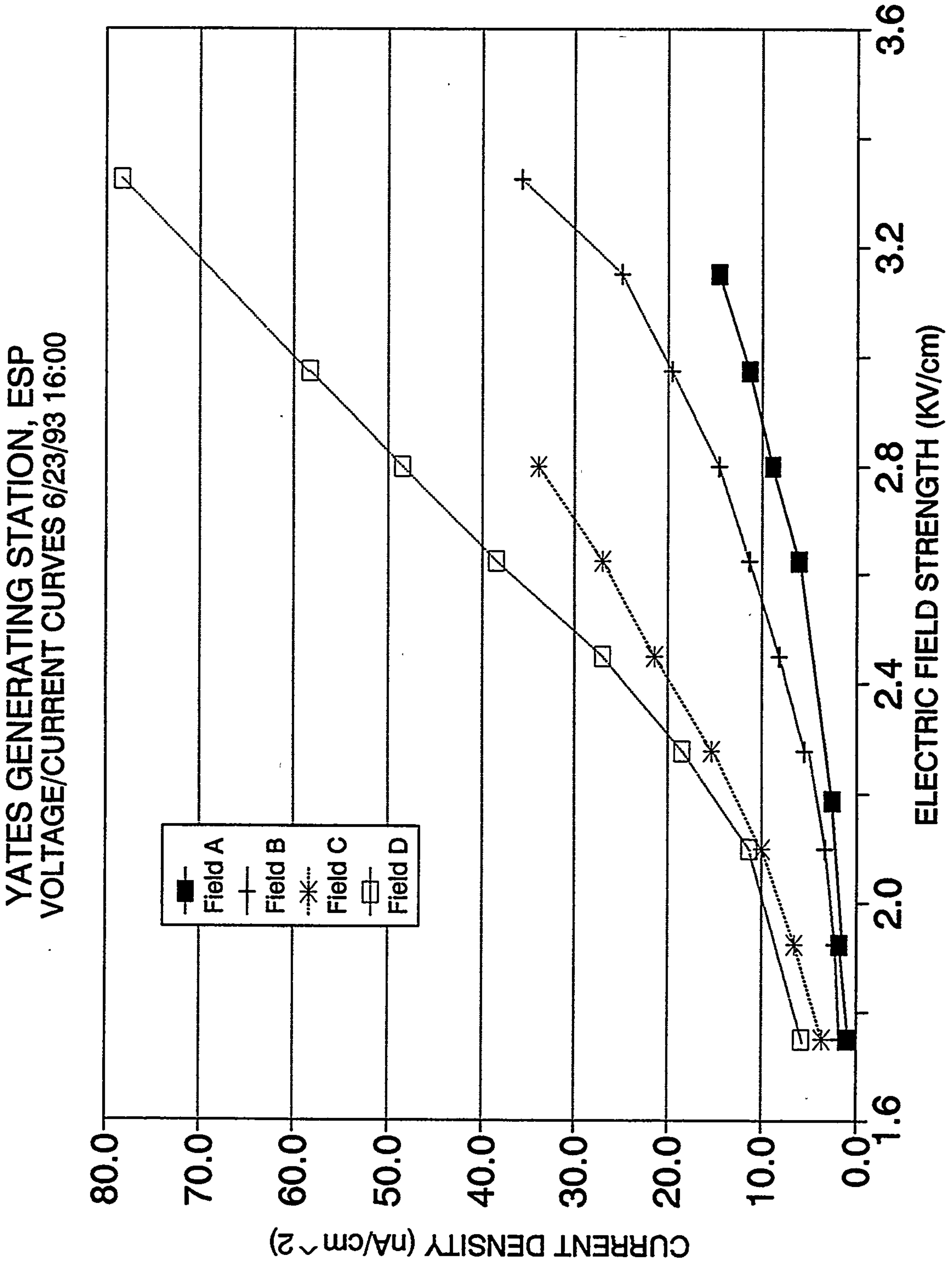

Figure 8-6
Voltage Current Curves

Field C is sparked at 2.8 kV/cm which is lower than the field strengths in Fields B and D which are upstream and downstream of Field C. Since the low voltage sparking is isolated in only one section of the ESP, the problem is probably not related to particle resistivity and is most likely due to some minor misalignment in this field.

Opacity. The opacity over a given period of time is shown in Figure 8-7 which is a plot of 6 minute averages of 15 second readings. During the time period shown in this figure, all sections should have been rapped. The lack of rapping spikes is likely due to the sampling time on the data recorder. However, it could be possible that the rapping spikes are relatively small. The holding force on the collected dust layer is proportional to the square of the particle resistivity. At the resistivity levels measured for this ash, the holding force could be strong enough to inhibit removal of the dust from the plates.

Predicted ESP Performance. The performance of the ESP was predicted using a predictive ESP computer model developed by ADA Technologies for DOE.[4] The non-ideal factor for gas flow distribution (25%) that has been recommended by EPRI for older ESPs was used in the modeling. The EPRI value for sneakage was modified for this application to take into account the fact that there were four electrical sections but only three mechanical sections.

The results of the predictions are shown in Table 8-2. As can be seen, the predicted performance of the ESP matches well with the measured performance. The model predicted 98.4% for the overall collection efficiency which agrees with the measured results from the total particulate tests. The outlet size distributions are also similar as both show a mass median diameter of approximately 4 μm. The opacity values are a little different, but the exact dimensions of the duct where the opacity is measured is not known. This is important for predicting opacity.

Figure 8-8 is a plot of the measured and predicted penetration as a function of particle size. The measured efficiency is much cruder because only 4 data points are available for the calculation from the inlet measurements. However, the measured and predicted efficiencies as a function of particle size are nearly identical. Both show a maximum penetration for submicron particles of 6 to 7 percent.

From the fact that there is a strong correlation between the measured and modeled performance, it is concluded that the ESP is performing as would be expected for the fly ash and flue gas conditions present. No operational or performance problems are observable.

Metals Removal Across ESP

Table 8-3 shows the removal of particulate metals across the ESP as well as the penetration of particulate metals through the ESP. The average penetration is 1.6% for all particles. As can be seen, most of the metals are removed at approximately the same rate as the total particulate. This would be expected because the metals are associated with all sizes of particles and the ESP is showing very high collection efficiency for even submicron particles. Figure 8-9 shows the distribution of metals as a function of particle size measured at the inlet

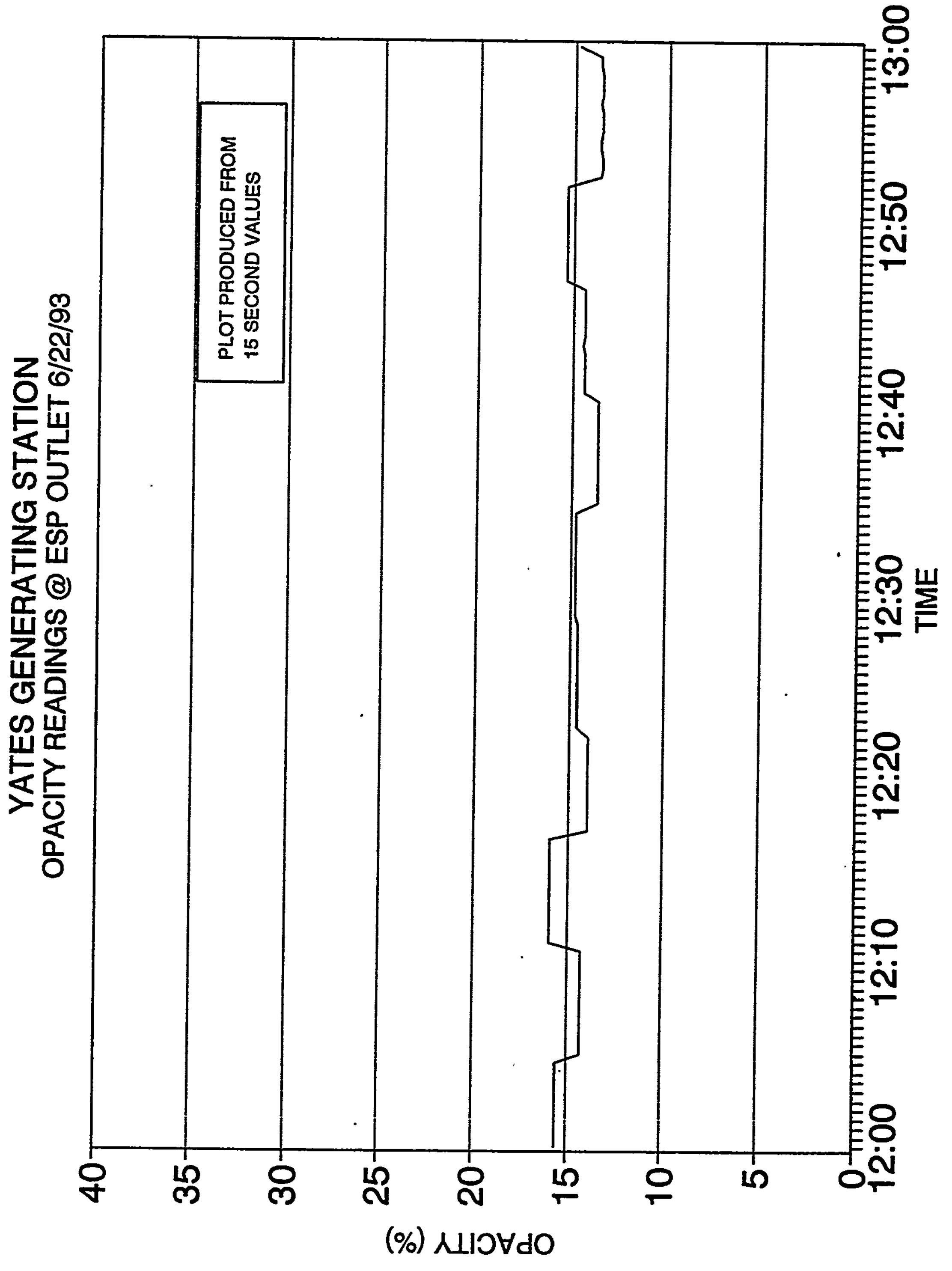

Figure 8-7
Opacity

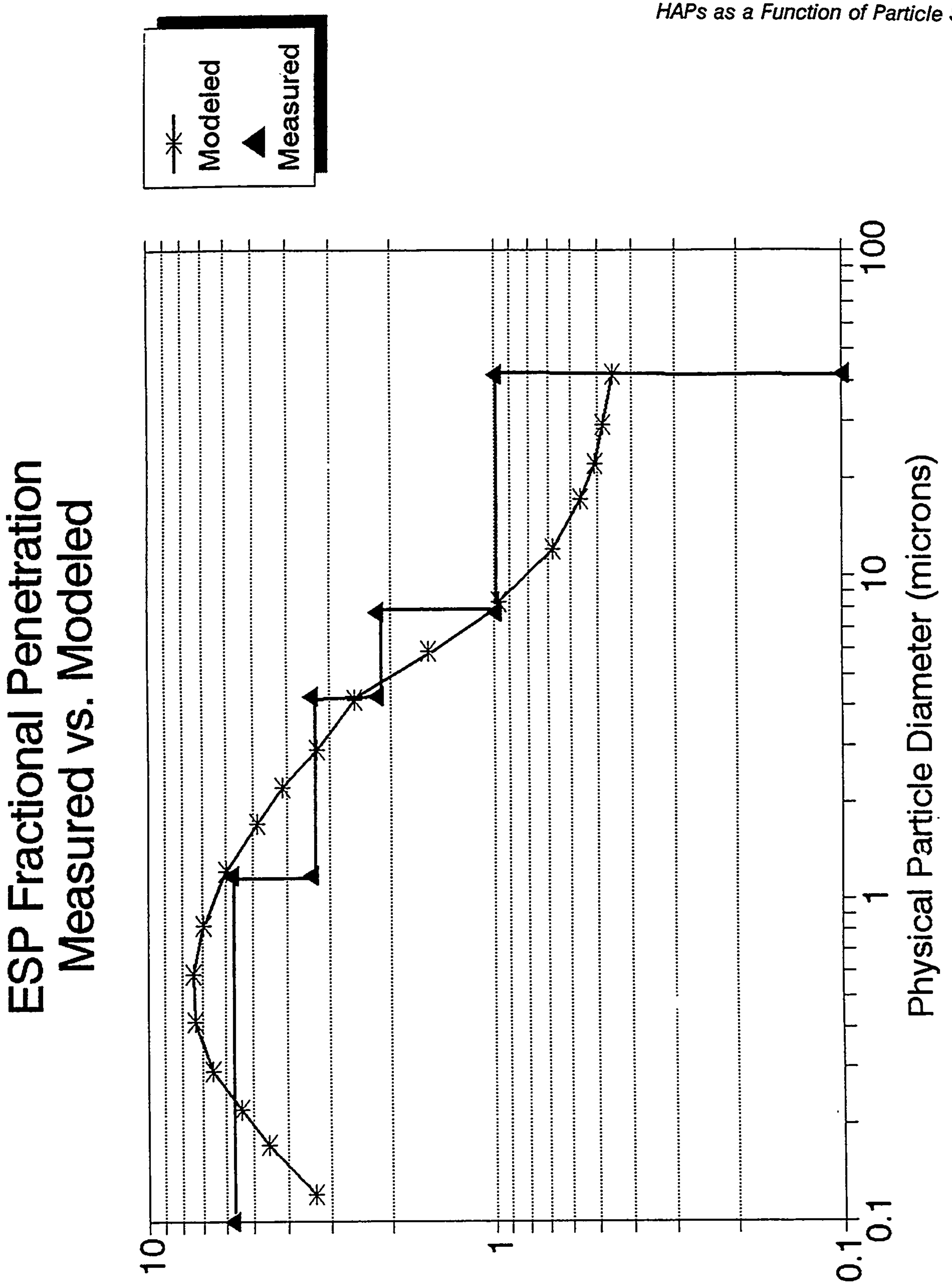

Figure 8-8
ESP Fractional Penetration

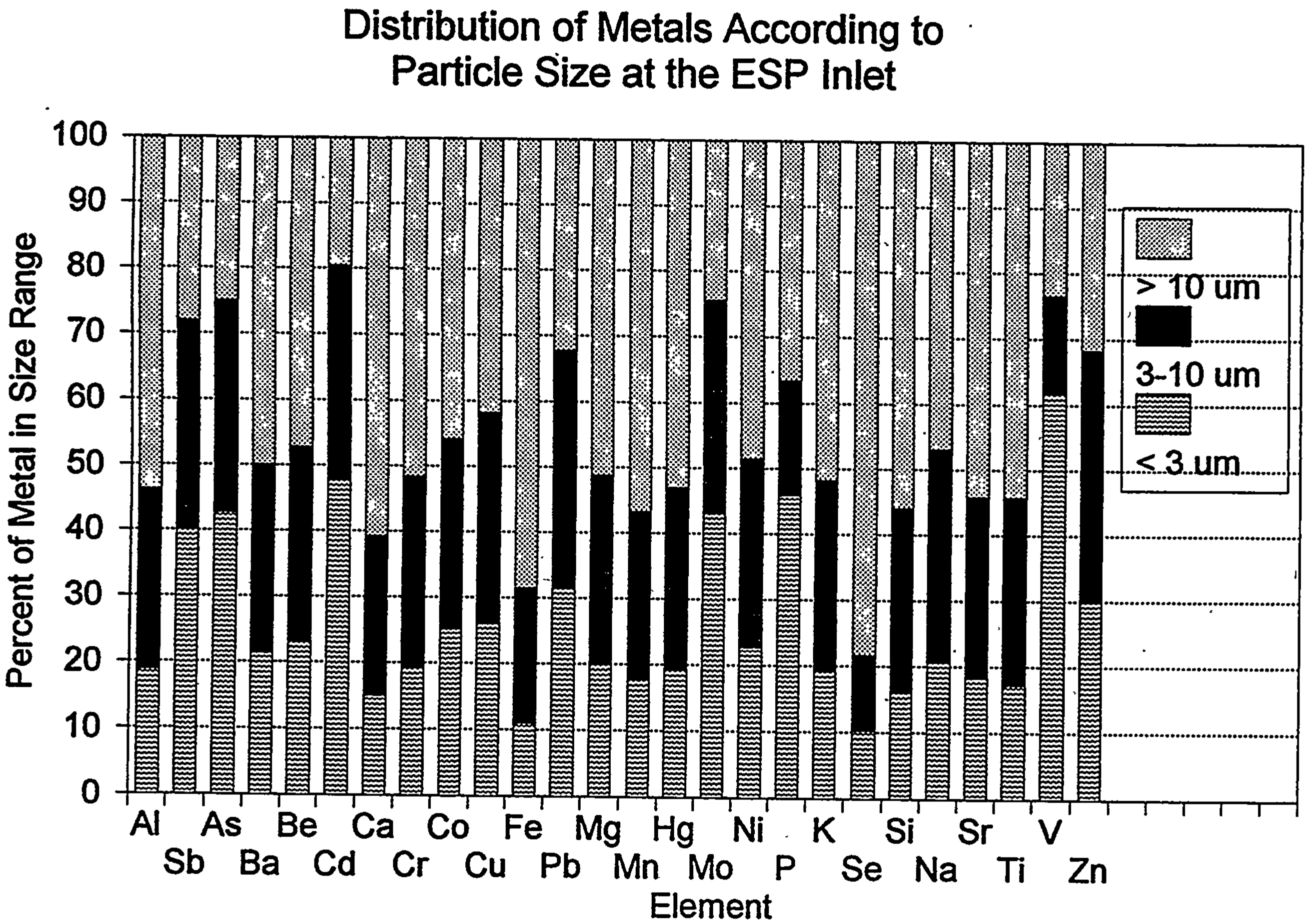

Figure 8-9
Distribution of Metals According to Particle Size at the ESP Inlet

Table 8-2
Comparison of Predicted and Measured ESP Performance

	Predicted	Measured
Collection Efficiency	98.4	98.4
Outlet Size Distribution		
Mass Median Diameter, μm	3.9	4.1
Standard Deviation	3.3	3.1
Opacity	19%	16%

to the ESP. As can be seen, as much as 50 to 70% of all particles are associated with very large particles (i.e., >10 μm).

Figure 8-10 is a similar plot of the distribution of the metals measured at the outlet. At the outlet, the highest concentration of mass is in the finest particles (i.e., <3 μm). This is due to the fact that the efficiency of the ESP drops off slightly as a function of particle size as shown in Figure 8-8.

Four Metals with Higher Penetration than the Average

There are four metals that have penetration values at least twice that of the overall average penetration. The increased penetration in arsenic (3.96%), cadmium (4.46%), and phosphorus (4.83%) [and mercury if substitution of sluiced ash concentration for the ESP inlet is used (10.98%)] are relatively small and could be due to either the low concentrations for arsenic and cadmium, or they could be due to the fact that they might be associated with the submicron particles. Both the measured and the predicted penetration of submicron particles was on the order of 6% so any increased enrichment of the fine particles for these particles could account for the higher penetration. The measured distribution at the outlet also points to an enrichment of the fine particles for these metals. Figure 8-10 shows that for arsenic, cadmium, and phosphorus, there is a greater percentage of the metal in the finest particles.

Selenium is the one metal which cannot be explained by the performance of the ESP. If all the selenium were associated with the most difficult to collect particles, <1 μm, it would have a maximum penetration of less than 7 percent. However, the measured penetration is greater than 50 percent. In addition, Figure 8-10 shows that nearly 50% of the selenium being emitted is associated with particles greater than 10 μm. This points to an error in sampling and analysis because it would not be physically possible for any particulate-phase material to penetrate the ESP at a rate of 50%, especially very large particles. Previous testing observation indicates that vapor-phase selenium may precipitate on the active sites provided by the filter in the Method 29 train under certain conditions. If this was the case at Plant Yates, the "penetration" could actually be caused by vapor-phase selenium which has been characterized as in the particulate phase.

Table 8-3
ESP Particulate-Phase Metals Collection Efficiency

	ESP Inlet		ESP Outlet		Efficiency	Penetration
Metal	μg/Nm³	lbs/hr	μg/Nm³	lbs/hr	(%)	(%)
Aluminum	870,000	926	12,100	12.9	98.60	1.40
Antimony	33	0.035	0.39	0.0004	98.81	1.19
Arsenic	404	0.43	16	0.017	96.04	3.96
Barium	4,440	4.72	74	0.079	99.33	1.67
Beryllium	93	0.10	1.65	0.002	98.23	1.77
Cadmium	24	0.03	1.07	0.001	95.54	4.46
Calcium	161,000	172	1,777	1.9	98.90	1.10
Chromium	2,870	3.05	23	0.024	99.20	0.80
Cobalt	275	0.29	4.45	0.005	98.38	1.62
Copper	768	0.82	16	0.017	97.92	2.08
Iron	808,000	860	8,537	9.1	98.94	1.06
Lead	768	0.82	18	0.019	97.66	2.34
Magnesium	42,100	45	657	0.70	98.44	1.56
Manganese	2,120	2.3	34	0.036	98.39	1.61
Mercury	(1.33)[a]	0.01	0.13	0.0002	90.2	10.98
Molybdenum	315	0.34	8.09	0.009	97.43	2.57
Nickel	2,030	2.16	22	0.023	98.92	1.08
Phosphorus	2,070	2.20	100	0.11	95.17	4.83
Potassium	157,000	167	2,150	2.3	98.63	1.37
Selenium	133	0.14	82	0.087	38.35	61.65
Sodium	45,800	49	803	0.85	98.25	1.75
Strontium	2,906	3.09	43	0.046	98.52	1.48
Titanium	55,100	57	757	0.81	98.63	1.37
Vanadium	2,761	2.9	54	0.057	98.04	1.96

[a] As discussed in Sections 6 and 7, the mercury concentration ESP inlet particulate sample appears to be high. The mercury concentration from the sluiced ash sample has been substituted here.

Notes:

1. Average inlet flow rate = 284,000 dscfm.
2. Average outlet flow rate = 284,000 dscfm.

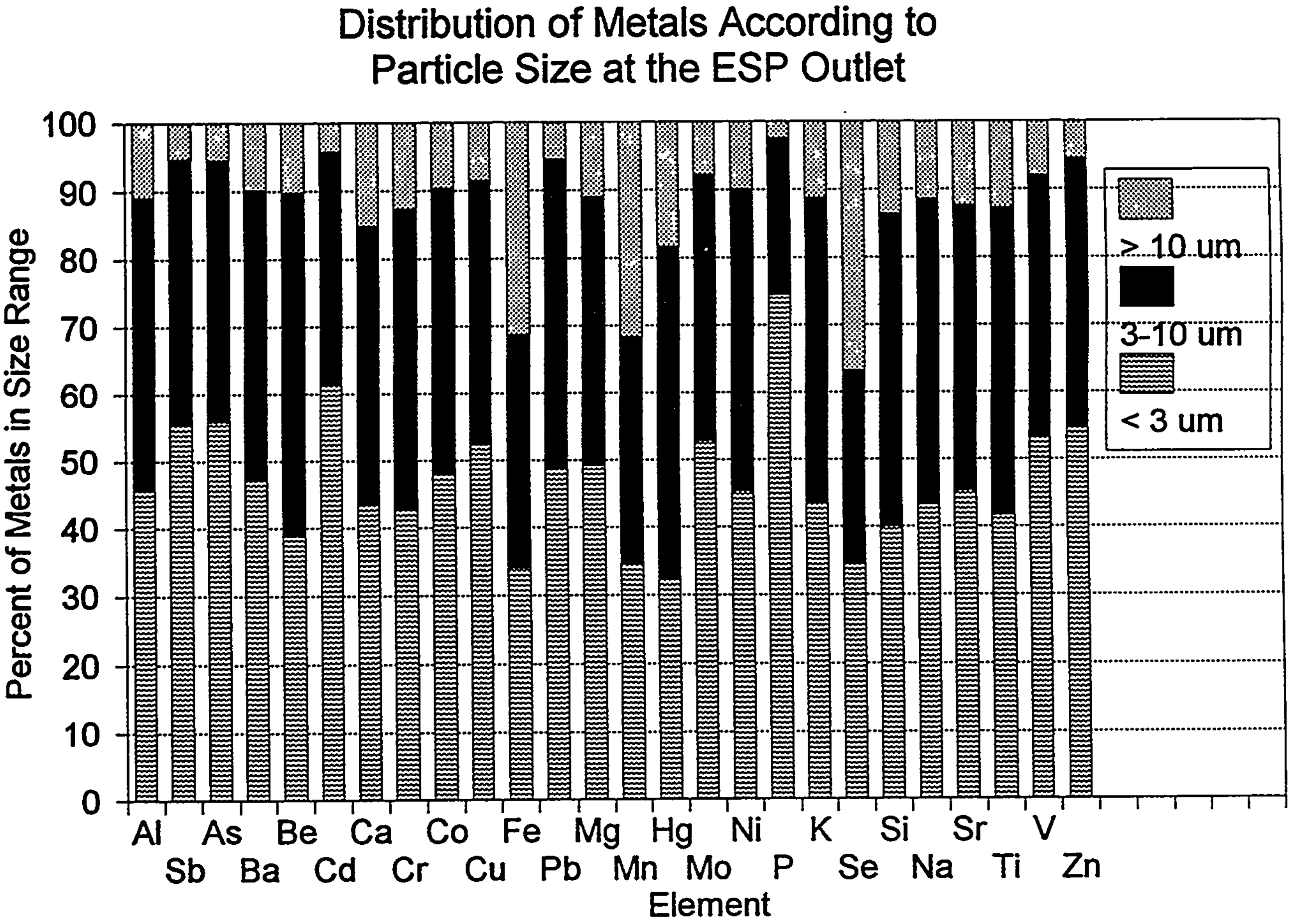

Figure 8-10
Distribution of Metals According to particle Size at the ESP Outlet

Further confusing this issue is the fact that particulate selenium also showed up on particles collected in the cyclones. The flow in the cyclones does not provide the intimate contact between the gas and collected particles that the filter does. However, it does appear that whatever phase shift occurring in Method 29 for selenium is also occurring in the cyclones.

Hopper Distribution

The concentrations of the metals in the hopper ash were also analyzed to determine if any insight could be obtained from this information relative to the performance of the ESP and HAPs. It has been hypothesized that if the metals were concentrated in the finer particles, which are more difficult to collect, then the downstream hopper might have a higher concentration of metals. The concentrations of metals in the particulate collected in the second hopper were divided by the concentrations from the first hopper to verify this hypothesis.

These data are plotted in Figure 8-11. As shown, the metals are distributed about a ratio of 1 with most metals increasing in the downstream hopper (ratio greater than 1). This supports the hypothesis of metals concentrating in the finer particles.

Another way to visualize the interplay between elemental concentration as a function of particle size and elemental enrichment produced by the ESP is to present concentration and enrichment together. Figure 8-12 does this. The vertical scale is enrichment of elements in the particulate material from the ESP inlet to the ESP outlet. The horizontal scale is the ratio of fine particle concentration to coarse particle concentration at the ESP inlet. Note that selenium has been left off the figure. Selenium's coordinates are (0.7, 12.09) which puts it in the far upper left corner of the plot. This implies that selenium is enriched in the ESP outlet particulate but not in the fine fraction of the ESP inlet ash. This result is probably biased by vapor-phase selenium precipitating or reacting on the Method 29 filter as previously discussed. However, the lower selenium concentration in the finer fractions of the ESP inlet ash was also unexpected given the volatile nature of selenium.

The figure shows, with the exception of selenium, a relatively smooth relationship between the two ratios. The plot demonstrates the concept that the elements, which at the ESP inlet have higher concentrations in fine particles than in coarse particles, becomes enriched at the ESP outlet in comparison with the ESP inlet.

Table 8-4 shows enrichment of inorganic elements in the different ash streams at Plant Yates. The factors were determined by dividing the concentration of an element in an ash stream by the coal ash concentration (concentration of an element in the coal divided by the ash fraction). These data generally show the trends expected with the more volatile elements exhibiting greater enrichment ratios in the ESP outlet than in the ESP inlet. (Chloride and fluoride show very little enrichment in the ash streams since the large majority of these elements are in the vapor phase.)

Of particular note is that most elements have significantly lower enrichment ratios in the stack particulate matter than in the ESP outlet ash. Using the major species' (aluminum,

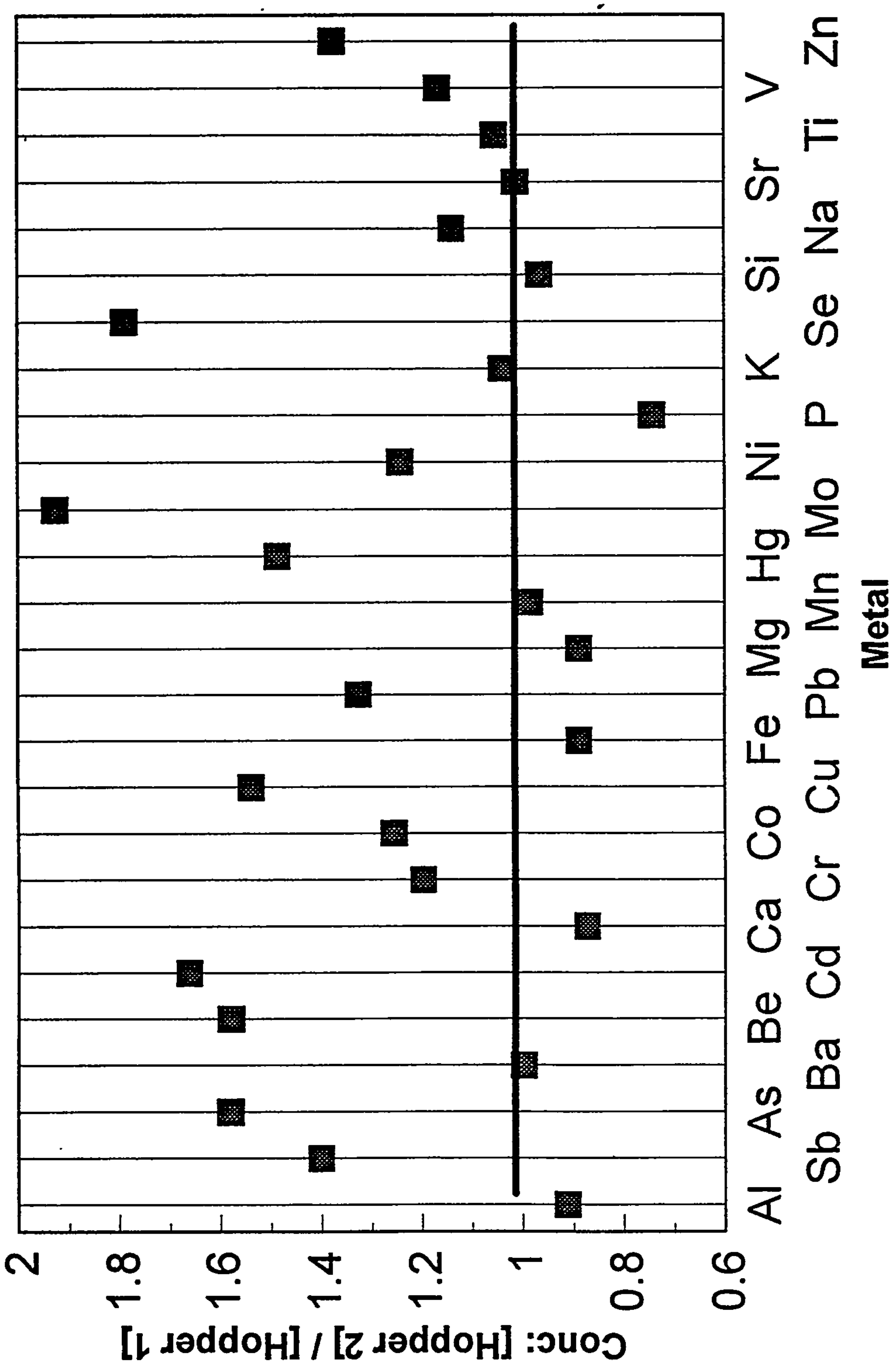

Figure 8-11
Total Metals Collection in Hopper

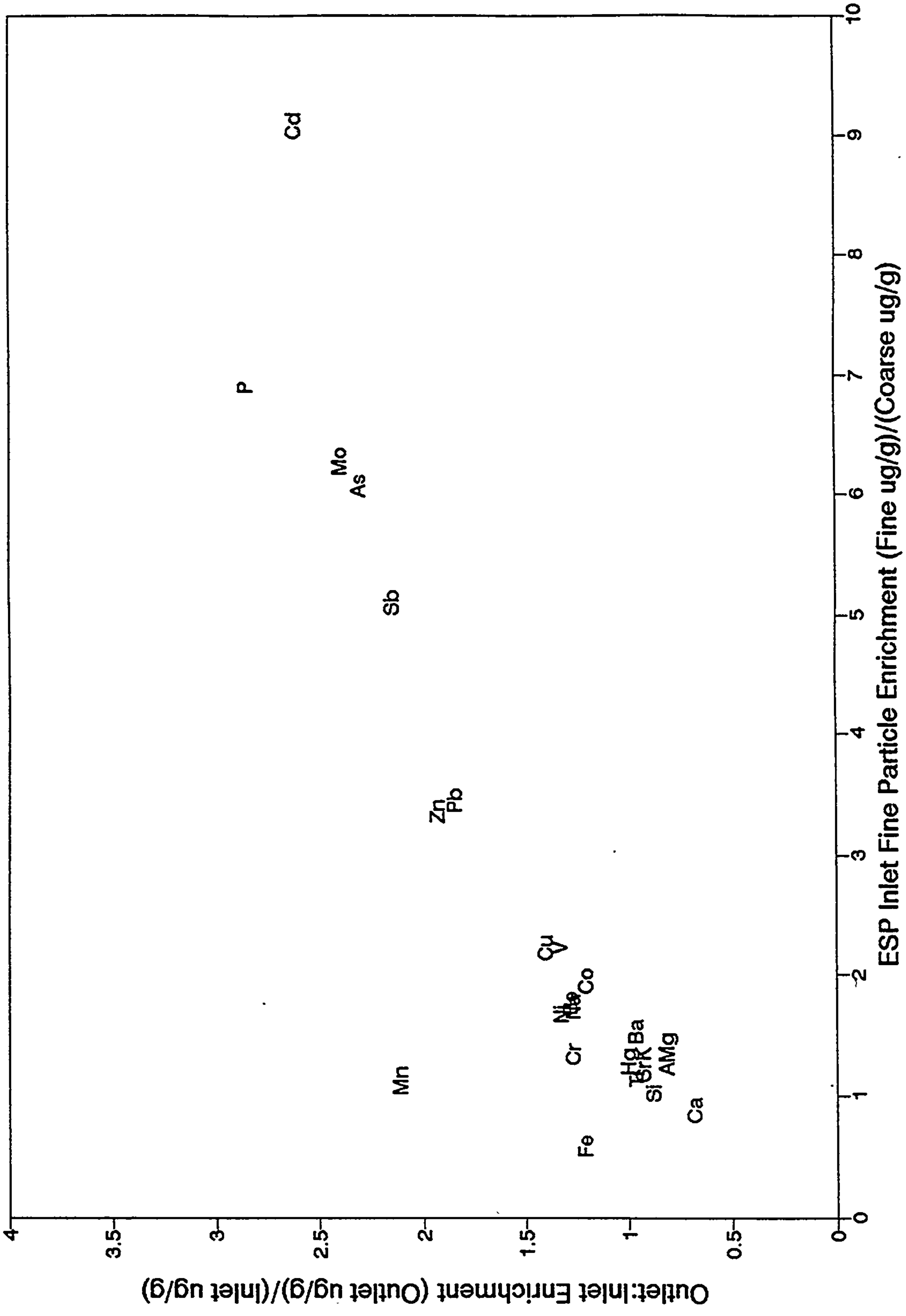

Figure 8-12
Elemental Relationship Between Outlet/Inlet Enrichment and Fine/Coarse Enrichment

Table 8-4
Enrichment of Streams in Inorganic Elements

	Coal Ash [a]	Bottom Ash		ESP Inlet Ash		Sluiced Ash		ESP Outlet Ash		Stack Particulate Matter	
Element	(µg/g)	(µg/g)	Enrichment	(µg/g)	Enrichment	µg/g	Enrichment	(µg/g)	Enrichment	(µg/g)	Enrichment
Aluminum	130,000	76,000	0.58	97,000	0.74	98,000	0.75	100,000	0.77	13,000	0.10
Antimony	5.50	1.1	0.21	3.6	0.66	3.4	0.62	2.7	0.50	3.8	0.69
Arsenic[b]	21.0	7.2	0.34	45	2.14	61	2.89	120	5.57	81	3.86
Barium	720	460	0.63	490	0.69	500	0.69	620	0.86	210	0.30
Beryllium	9.91	7.7	0.77	10	1.05	11	1.12	14	1.41	3	0.30
Boron	900	280	0.31	N/A	N/A	470	0.53	N/A	N/A	N/A	N/A
Cadmium[b]	2.7	0.32	0.12	2.7	0.99	4.1	1.52	8.9	3.30	41	15.17
Calcium	19,000	20,000	1.05	18,000	0.94	14,000	0.71	15,000	0.77	19,000	0.97
Chloride[c]	11,200	130	0.01	680	0.06	50[d]	0.00	317	0.03	15,000	1.34
Chromium[b]	223	190	0.86	320	1.42	190	0.83	190	0.86	330	1.47
Cobalt	31.6	32	1.00	31	0.98	37	1.17	37	1.17	19	0.59
Copper[b]	330	77	0.24	86	0.26	100	0.32	120	0.36	56	0.17
Fluoride[c]	901	32	0.03	0.15	0.00	99	0.11	0.85	0.00	3.5	0.00
Iron	100,000	130,000	1.27	91,000	0.88	84,000	0.82	61,000	0.59	12,000	0.11
Lead[b]	72	20	0.28	79	1.10	83	1.15	150	2.12	36	0.50
Magnesium	5,100	3,600	0.71	4,700	0.92	4,900	0.96	5,500	1.07	2,800	0.55
Manganese	210	270	1.28	240	1.12	250	1.16	240	1.15	490	2.31
Mercury[c]	0.72	0.01[d]	0.01	0.79	1.10	0.15	0.20	0.9	1.25	0.57	0.79
Molybdenum[b]	200	3.0[d]	0.01	35	0.17	7.2[d]	0.04	58	0.29	73	0.36
Nickel[b]	270	130	0.48	230	0.84	140	0.53	160	0.58	2,500	9.28
Phosphorus	760	400	0.52	230	0.30	68	0.09	830	1.09	110	0.14
Potassium	30,000	14,000	0.48	17,000	0.59	18,000	0.61	18,000	0.60	2,900	0.10
Selenium[c]	21	0.57[d]	0.03	15	0.71	12	0.57	570	27.35	3,500	166.50
Sodium	5,700	3,600	0.64	5,100	0.90	5,100	0.89	6,700	1.18	1,900	0.34
Strontium	670	280	0.41	320	0.48	320	0.48	360	0.53	110	0.16
Titanium	8,100	5,600	0.69	6,100	0.76	6,300	0.79	5,400	0.67	910	0.11
Vanadium	350	280	0.78	310	0.87	330	0.92	380	1.07	110	0.32
Sulfate		1,590		8,900			3,450	30,000		410,000	

[a] Coal ash concentrations were calculated by using coal concentrations and dividing by the coal ash fraction.
[b] Denotes an element that is vaporized in the boiler and then condenses and may become enriched on fine particles. Cr & Ni do not always show enrichment.
[c] Denotes an element that is vaporized and can remain in the vapor phase. Selenium can either be enriched in the fine particles or be in the gas phase.
[d] The measured concentrations were below detection limit. Numbers shown are half of the detection limit.

iron, magnesium, potassium, sodium, and titanium) concentrations, it appears that only about 25% of the mass in the stack particulate was fly ash. The bulk of the mass (about 65%) can be attributed to sulfuric acid mist (based on the large increase in sulfate), while gypsum carryover accounts for about 5% and liquid chloride carryover accounts for about 3 percent. Note that these results indicate a flue gas SO_3 concentration of 1-2 ppm, which is in the same low range as that measured in the flue gas in the ESP (0.3 ppm).

Elements that show enrichment in the stack particulate matter (other than calcium [from gypsum] and chloride) are selenium, nickel, manganese, chromium, and cadmium. Problems with selenium have been discussed in this section. The nickel and chromium concentrations in the stack include one high concentration which does not appear to be consistent with other ash numbers. Their enrichment ratios become much more reasonable when these values are excluded. The reason for the apparent high manganese and cadmium enrichments is not known.

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9

MERCURY METHODS COMPARISON AND SPECIATION DETERMINATIONS

This section compares the results of two different methods used to determine the concentrations of total mercury and its various chemical forms in the flue gas streams. The objectives of the mercury sampling were to determine total mercury concentration and individual mercury species concentrations at each of the three flue gas sampling locations. These results will provide information on the emissions and control of mercury. In addition, the speciation results can be used to more accurately assess the possible health risks associated with mercury emissions.

Two different methods were used to measure mercury concentrations in the flue gas. The Bloom mercury speciation train[1] was used to measure the concentrations of individual vapor-phase mercury species: ionic mercury and elemental mercury. Total mercury, including both particulate and vapor phases, was measured using the proposed EPA Method 29 multi-metals train. Although the Method 29 multi-metals train was designed to measure total concentrations of metals and not to provide speciation information, it may still provide some insight into the vapor-phase mercury species present.

Sample Collection and Analysis

This subsection describes the sampling and analytical methods used to measure mercury concentrations. The methods are described in detail in Appendix B, but the important features are discussed here. In addition, the sample collection schedule is presented.

Methods and Conditions

Bloom Speciation Train. The Bloom mercury speciation train was used to collect samples at the ESP inlet, the ESP outlet, and the stack. A quartz-lined probe was inserted into each duct, and flue gas was extracted non-isokinetically at a single point. The flue gas then passed through a series of four solid adsorbent cartridges which were used to trap the various vapor-phase mercury species. The cartridges were maintained at approximately 110°C in a heated jacket outside the duct. The first two cartridges contained KCl-impregnated soda lime, which is designed to capture ionic mercury species (Hg^{+2} and Hg^{+}). The third and fourth cartridges contained iodated carbon, which is designed to capture elemental mercury. A glass wool plug ahead of the adsorbent cartridges prevented particulate from entering the adsorbents. This plug was not analyzed, because the single-point, nonisokinetic sampling does not provide representative particulate capture. Only vapor-phase species were determined.

The KCl/soda lime traps were dissolved in acetic acid solutions. Ionic mercury was determined by aqueous-phase ethylation, purging onto a carbotrap, cryogenic GC separation, and detection with cold vapor atomic fluorescence spectrometry (CVAFS). This method was used to quantify methyl mercury (MMHg), as methylethyl mercury, however this technique was discovered to produce artifacts (see letter from Frontier Geosciences at the end of this section) due to a reaction during the dissolution of the KCl/soda lime traps. All data for methyl mercury derived using this method is considered in error and has been disregarded. Inorganic ionic mercury (Hg^{+2}) was determined as diethyl mercury. Elemental mercury on iodated carbon traps was determined by digesting with a mixture of HNO_3/H_2SO_4 and BrCl, reducing with $SnCl_2$, purging and preconcentrating on gold, and detecting with CVAFS.

Several QA/QC procedures were used for the Bloom train. Field blanks were collected at each of the three sampling locations to assess the effects of contamination. A trip blank was also analyzed. Laboratory spikes were performed for each type of mercury species to assess analytical efficiency. In addition, the CVAFS instrument was calibrated using certified standards.

Method 29 Multi-Metals Train. The multi-metals trains were used to collect samples at the ESP inlet, the ESP outlet, and the stack. The trains used at the ESP outlet and stack were Method 5 trains, with particulate collected on a quartz filter maintained at constant temperature (approximately 250°F) outside of the duct. Because of the high particulate concentrations at the ESP inlet, a Method 17 train was used, with particulate collected in an in-situ quartz thimble. At all three locations, samples were collected isokinetically while traversing the duct according to Method 1.

The impinger trains, used to collect vapor-phase metals, were identically configured at each location. The first and second impingers contained a 5% HNO_3/10% H_2O_2 solution. The third impinger was empty, to prevent any mist carryover. The fourth and fifth impingers contained a 10% H_2SO_4/4% $KMnO_4$ solution.

Particulate samples were microwave-digested in HF/aqua regia solutions and analyzed for all target metals. Mercury concentrations were determined using cold vapor atomic absorption spectrometry (CVAAS). The HNO_3/H_2O_2 solutions were also analyzed for all target metals, with the mercury determined by CVAAS. The $H_2SO_4/KMnO_4$ solutions were analyzed only for mercury using CVAAS.

The multi-metals train may provide information on mercury speciation. Ionic forms of mercury are water-soluble and should be readily captured in the HNO_3/H_2O_2 solution. Elemental mercury, on the other hand, should pass through the HNO_3/H_2O_2 impingers, because the solubility of elemental mercury in aqueous solutions is very low and the H_2O_2 cannot efficiently oxidize it. The elemental mercury will be oxidized and captured in the $H_2SO_4/KMnO_4$ impingers.

Several QA/QC procedures were followed for the multi-metals trains. Field blanks, reagent blanks, and method blanks were analyzed to assess the effects of contamination. Matrix-spiked and matrix-spiked duplicate samples were analyzed to assess recovery and precision.

The CVAAS instruments were calibrated using certified standards, and calibration checks were routinely performed.

Samples Collected

Figure 3-2 shows the collection schedule for the Bloom train and multi-metals train samples. Three samples were collected for each train type at each of the three sampling locations. Gas sample volumes were approximately 0.1 Nm^3 for the Bloom train and 3 Nm^3 for the multi-metals train. Field data sheet summaries are included in Appendix C.

Data Analysis

Table 9-1 shows the mercury concentrations measured with the Bloom train and the Method 29 multi-metals train. The total vapor-phase mercury concentrations measured using the two techniques are in good agreement. Using the mean multi-metals train results, it appears that approximately 99% of the particulate-phase mercury is removed by the ESP, and the removal of total mercury by the scrubber is approximately 46%.

The speciation results from the two methods show similar trends. Ionic mercury is the predominant species in the ESP inlet and ESP outlet gas streams, but the ionic mercury is more efficiently removed by the scrubber, as shown by its markedly lower concentrations at the stack. The removal of ionic mercury by the scrubber can be attributed to a higher solubility in water as compared to elemental mercury.

While the overall trends in the two methods are similar, the detailed speciation results do not appear equivalent. In particular, the levels of elemental mercury measured by the two techniques do not agree well at any of the three locations, and the agreement is poor between the two techniques for ionic mercury concentrations at the stack.

Table 9-2 shows the mercury concentrations found in the blank samples and their significance relative to the actual sample concentrations. Blank contamination does not appear to be significant. Table 9-3 summarized the spike recoveries for the two techniques. All of the recoveries were within the acceptable range of 75 to 125 percent.
While the QA/QC results for the two techniques indicate acceptable quality, they only address the issues of contamination and analytical accuracy. The issue of species conversion during sampling has not been addressed. Therefore, while each method can be considered to give reliable results for the total concentration of vapor-phase mercury, less confidence can be placed in the speciation results. The possibility of conversion of one species to another within the sampling equipment or in the sampling media make it less certain that the species were actually present in the flue gas at the measured levels.

Table 9-1
Mercury Concentrations in Flue Gas

		Concentrations, $\mu g/Nm^3$					
Location	**Component**	**Run 1**	**Run 2**	**Run 3**	**Mean**	**95% CI**	**% of Vapor**
Bloom Hg Speciation Train[a]							
ESP Inlet	Ionic Hg	4.5	3.8	5.0	4.4	1.5	69
	Elemental Hg	2.4	2.4	1.2	2.0	1.7	31
	Total Vapor	6.9	6.2	6.2	6.4	1.0	–
ESP Outlet	Ionic Hg	5.8	4.6	4.0	4.8	2.3	66
	Elemental Hg	2.5	2.6	2.4	2.5	0.2	34
	Total Vapor	8.3	7.2	6.4	7.3	2.4	–
Stack	Ionic Hg	0.38	0.51	0.63	0.47	0.33	15
	Elemental Hg	3.0	3.1	2.3	2.8	1.1	85
	Total Vapor	3.4	3.6	2.9	3.3	0.9	–
Method 29 Multi-Metals Train							
ESP Inlet	Ionic Hg[b]	4.6	4.9	5.7	5.1	1.5	94
	Elemental Hg[c]	0.51	0.31	0.23	0.35	0.36	6
	Total Vapor	5.1	5.3	6.0	5.4	1.2	–
	Solid	5.2	9.6	6.4	7.1	5.6	–
	Total Vapor + Solid	10.3	14.8	12.4	12.5	5.6	–
ESP Outlet	Ionic Hg	4.8	4.1	4.9	4.6	1.1	82
	Elemental Hg	1.2	1.1	0.65	0.98	0.73	18
	Total Vapor	6.0	5.2	5.5	5.6	1.1	–
	Solid	0.11	0.12	0.14	0.13	0.04	–
	Total Vapor + Solid	6.1	5.3	5.7	5.7	1.1	–
Stack	Ionic Hg	1.1	1.5	1.9	1.5	0.9	50
	Elemental Hg	1.8	1.6	1.2	1.5	0.7	50
	Total Vapor	2.9	3.1	3.1	3.0	0.3	–
	Solid	<0.0050	0.0116	<0.0051	0.0056	0.013	–
	Total Vapor + Solid	2.9	3.1	3.1	3.0	0.3	–

[a] Although MMHg values were originally reported by Frontier Geosciences, a letter from Frontier Geosciences was issued on January 26, 1994 stating, in part, "... we now know that the MMHg we were measuring and reporting is due to an artifact. [this method] ... overestimates the amount of MMHg. The MMHg fraction should tentatively be considered as part of the Hg(II) fraction of the total Hg in flue gas until our ongoing investigations are completed." These investigations are still in progress and, until they are completed, the presence or absence of MMHg in the flue gas cannot be confirmed.

[b] Mercury collected in the HNO_3/H_2O_2 impingers.

[c] Mercury collected in the $H_2SO_4/KMnO_4$ impingers.

Table 9-2
Summary of Blank Results

Blank Sample Type	No. of Blanks	Range of Blank Levels	Max Contribution to Samples[a]
Bloom Train			
Ionic Hg			
Field Blanks	6	0.3-0.6 ng	4%
Trip Blanks	2	0.5-0.8 ng	4%
Elemental Hg			
Field Blanks	6	1.3-4.6 ng	4%
Trip Blanks	2	1.1-3.7 ng	3%
Method 29 Multi-Metals Train			
HNO_3/H_2O_2 Impingers			
Field Blanks	3	<0.24 μg/L	<5%
Reagent Blanks	1	<0.24 μg/L	<5%
$H_2SO_4/KMnO_4$ Impingers			
Field Blanks	3	<0.24 μg/L	<28%
Reagent Blanks	1	<0.24 μg/L	<28%

[a] Maximum blank value as a percentage of the minimum sample result.

Table 9-3
Summary of Spike and Audit Sample Recoveries

Sample Type	No. of Samples	Range of Recoveries
Bloom Train		
Ionic Hg	2	102 - 103%
Elemental Hg	2	100 - 102%
Method 29 Multi-Metals Train		
HNO_3/H_2O_2 Impingers	2	120%
$H_2SO_4/KMnO_4$ Impingers	2	76 - 78%

The Bloom train is a technique that is still being developed.[2] Extensive work has been done to improve the capture efficiency of the traps, to increase the analytical efficiency, and to minimize the chance for species conversion. There are no studies that would conclusively demonstrate the validity of the method, such as the spiking of specific mercury compounds into the flue gas ahead of the sampling train. Therefore, the method can be considered unproven.

There is no published information regarding the ability of the multi-metals train to provide mercury speciation information from utility stack gases. The interpretation of the results thus far relies solely on chemical theory. In addition, the extent of species conversion within the train is unknown.

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January 26, 1994
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Discovery of Methyl Mercury Artifact in the Solid Sorbent Speciation (S ^{3}) method for Coal Combustion Fluegas

We have stated in both reports and presentations (Prestbo and Bloom, 1993, Bloom et al., 1993) that monomethyl mercury (MMHg) can be measured and is found in coal combustion flue gas in the range of 5-15% of the total Hg. Because of very recent experiments we have completed in the laboratory, we now know that the MMHg we were measuring and reporting is due to an artifact. Only through painstaking laboratory work were we able to discover the unusual chemical reactions which produce MMHg in solution. We discovered that Hg(II) and S(IV) collected on the KCl/soda lime sorbent, when digested in 10% acetic acid solution will form MMHg on the high pH surface of the dissolving soda lime. The likely mechanism leading to this can be found (in retrospect) in a paper by Lee and Rochelle (1987). This finding was quite surprising considering that SO_2 is known to be a reducing and not an oxidizing compound. The MMHg forms due to the release of methyl groups during the degradation of acetic acid in conjunction with the oxidation of $SO_3^=$.

What we can state convincingly is that all previous flue gas data generated by our laboratory overestimates the amount of MMHg. The MMHg fraction should tentatively be considered as part of the Hg(II) fraction of the total Hg in fluegas until our ongoing investigations are completed. It should also be clearly stated that although the MMHg values are no longer valid, this is not true for Hg(II), Hg^o and especially total Hg. Further, please refrain from stating that MMHg is *not* present in fluegas until we have a chance to complete some field site studies using a refined methodology.

We are actively pursuing the problem encountered. Initially we will investigate non-methyl containing solutions (i.e. citric acid) for dissolving KCl/soda lime to avoid the artifact. Secondly, we will use several other means of collecting flue gas, including unique impinger solutions to more conclusively determine the presence or absence of MMHg in combustion flue gas.

As you know, speciation of trace metals, and especially mercury is difficult in any matrix. We regret that previous MMHg fluegas data was in error. We will continue to communicate to you any of our new findings as we have with this one.

Please don 't hesitate to call us if you have any questions or need further clarification on this issue.

References

Bloom N.S., Prestbo E.M. and Miklavcic V.L. (1993) "Fluegas mercury emissions and speciation from fossil fuel combustion", presented at Conference on Managing Air Toxics: State of the Art, Washington D.C. July 13-15 (withdrawn from publication).

Lee Y.J. and Rochelle G.T. (1987) "Oxidative degradation of organic acid conjugated with sulfite oxidation in flue gas desulfurization: products, kinetics, and mechanism", Env. Sci. and Technol., 21:266.

Prestbo E.M. and Bloom N.S. (1993) "Recent advances in the measurement of mercury species in combustion flue gas using solid phase adsorption and cold vapor atomic fluorescence spectroscopy (CVAFS)", Presented at the AWMA 86th Annual Meeting, June 13-18, (93-TA-32.05).

10

HEXAVALENT CHROMIUM DETERMINATIONS

Introduction

The stack gas at Plant Yates was sampled for the presence of hexavalent chromium and total chromium. Hexavalent chromium samples were analyzed on site at Plant Yates in order to provide results as quickly as possible. Radian's experience has shown that hexavalent chromium is unstable and is reduced to trivalent chromium quite rapidly during the first 24 hours after sample collection. Appropriate blanks were analyzed to minimize the possibility that any contamination would go undetected.

Sample Collection and Analysis

Hexavalent chromium samples were collected on June 25, 26, and 27, 1993. Samples were collected and analyzed using EPA's recirculating caustic solution method.[1] This method uses a recirculating probe system that mixes the total gas sample (vapor and particulate) with the caustic impinger solution immediately after the sample nozzle. This provides a high pH environment to minimize the reduction of Cr^{6+}. Analysis was performed on site using an ion chromatograph. However, instrument problems were encountered and no useful data could be obtained.

As a result, the samples were returned to Radian's laboratory in Austin and analyzed for hexavalent chromium as well as total chromium. In addition, QA/QC samples were analyzed as follows:

- One matrix spike;
- One performance audit sample;
- Three field blanks; and
- One trip blank (total chromium only).

Although the hexavalent sample collection method was used as specified in the published method, it should be noted that the collection procedure for obtaining Cr^{6+} samples from a flue gas matrix containing SO_2 has not been validated.

Data Analysis

As shown in Table 10-1, hexavalent chromium and total chromium were nondetectable in the samples collected after appropriate blank correction had been applied.

Table 10-1
Results for Hexavalent Chromium and Total Chromium

Specie	Units	Run 1	Run 2	Run 3	Average
Chromium VI	$\mu g/Nm^3$	<0.18C	<0.19C	<0.20C	<0.190
Total Chromium	$\mu g/Nm^3$	<0.52C	<0.57C	<0.59C	<0.560

C = Data flag; value was blank-corrected below the detection limit.

Experience has shown that measurement of hexavalent chromium can be very difficult in electric utility flue gas. A brief discussion of the technical implications of determination of chromium (VI) in stack gas and, in particular, in combustion sources and utility sources is included here.

The Cr(VI) method depends on the solubility and stability of chromium (VI) in basic aqueous solution. The method calls for the use of a strong base in a solution contained in the impingers and recycled to the probe tip for early gas contact and flushing to the probe walls. The method is theoretically sound but has some limitations when applied to combustion sources in general and utility flue gases specifically.

As mentioned above, Cr(VI) is stable in a strong alkaline solution (pH > ~9). But all combustion gas streams contain large amounts of CO_2 (10-20%), which is an acid gas, and serves to lower the pH of the impinger solution. As a result, the pH may dip lower than desirable during sampling, or the solution must be more alkaline then specified in the method or continually monitored. As a further complication, utility flue gas contains significant levels of SO_2 (100 ppm or more). SO_2 is also an acid gas but is a reductant as well. So the impinger solution designed to absorb Cr(VI) also absorbs CO_2 and SO_2. The result of this is a lowered pH and a solution which contains an oxidant [Cr(VI)] and a reductant (SO_2/HSO_3^-). As the pH falls, the redox couple becomes more favorable, and any Cr(VI) present may be reduced by SO_2/HSO_3^- and not detected as Cr(VI).

References

1. 40 CFR 266, Subpart H, Appendix IX, "Methods Manual for Compliance with the BIF Regulations," Section 3.0, "Sampling and Analytical Methods," Subsection 3.2, "Determination of Hexavalent Chromium Emissions from Stationary Sources (Method Cr^{6+})," 7-1-91 edition.

11

DETERMINATIONS OF TOXICS ON PARTICLE SURFACES

The Clean Air Act Amendments of 1990 (CAAA) require that emissions of hazardous air pollutants (HAPs) from coal-fired power plants be evaluated for potential health risks. The 189 hazardous substances listed in the CAAA include numerous inorganic and organic species that remain volatile under the conditions present in flue gas emission control systems at coal-fired power plants. As the flue gas cools downstream of these control devices and is released into the atmosphere, it is hypothesized that many of these substances condense on the surface of the fine particulate matter not removed by the control device.

Fine-particulate emissions in the respirable size range of less than 10 microns are of particular interest in assessing health risks. The environmental and toxicological impacts resulting from these emissions are typically estimated on a "worst case" basis where the total composition of the emitted particles is considered available to biological and ecological systems. The condensed metal species found predominantly on the surface of fly ash particles are more accessible to the environment than those species trapped in the alumina-silica fly ash matrix. More appropriately, the leachability of these toxic substances and their availability relative to the total composition should be considered when assessing the health risks associated with particulate-borne HAPs.

Radian Corporation, under contract with the United States Department of Energy (DOE Contract No. DE-AC22-92PC90367), is conducting a separate test program to collect and analyze size-fractionated stack gas particulate samples for numerous inorganic HAPs. Specific goals of the program include collecting gram quantities of size-fractionated stack gas particulate matter (after a wet scrubber) and determining the relationship between particle size, bulk composition, and extractable (surface-leachable) composition.

At Plant Yates, extractable metal concentrations were determined on bulk, rather than size-fractionated samples of flue gas particulate matter. But in addition to sampling the gas from the JBR-FGD system, samples were also collected from the ESP inlet and outlet. From the data collected, the relationship between extractable metal emissions from both wet and dry particulate control devices is possible.

This section compares the analytical results for bulk composition and surface leachability of metals in flue gas particulate samples collected from the inlet and outlet of the ESP and from the outlet of the JBR-FGD system. Metal concentrations are reported for arsenic, barium, beryllium, cadmium, chromium, copper, cobalt, lead, manganese, molybdenum, nickel, selenium, and vanadium.

Sample Collection and Analysis

The difficulty in characterizing surface species is that there are currently no standard, certified methods documented for determining the leachability of metals from the surface of micron-sized particles. In a previous study, several leaching agents and analytical techniques were applied to standard reference fly ash samples for evaluation; three were selected for use on the entrained fly ash samples collected during this project. The techniques selected for characterizing surface availability involve acid leaching and digestion of the particulate samples followed by inductively coupled plasma-mass spectrometry (ICP-MS) analysis. For comparison, the total composition was derived from the metals analysis of the size-fractionated particulate matter at the ESP inlet and outlet, and from the analysis of the stack gas multi-metals train filter samples.

Sample Collection

Sample collection at the ESP inlet was performed according to EPA Reference Method 17[1] (in-stack filtration). Quartz-fiber thimble filters were specified to handle the high particulate mass loading encountered upstream of the ESP and to reduce the background levels of trace elements associated with glass-fiber filters. To avoid introducing filter media into the sample and providing blank analyses for background corrections, sample material was recovered directly from the thimble filters and prepared for analysis.

EPA Reference Method 5[2] was used to collect particulate matter from the ESP outlet and stack gas streams. Quartz-fiber filters were also specified; however, due to mis-identification, glass-fiber filters were inadvertently used on all extractable metals test runs at the ESP outlet and on Runs 1 and 3 at the stack location. Enough sample mass was collected on the ESP outlet filters to permit ash sample separation from the filter media; however, the small sample mass collected on the stack gas filters precluded this separation.

Sample Preparation and Analysis

Sample material recovered from the filters was split in 0.1 gram portions and prepared by the techniques described in Figure 11-1. Stack gas filters were split into three roughly equal fractions and weighed to determine each segment's percentage of the total filter mass. The particulate sample mass on each fraction was determined by multiplying this percentage by the filter weight gain representing the total sample mass. Uniform distribution of the sample mass and the mass of the filter media is assumed. Glass-fiber filter blanks were not prepared for analysis; however, a blank quartz-fiber filter was prepared and analyzed to assess the background levels of extractable metals specific to the quartz-fiber media.

An overview of the sample preparation and analysis techniques selected for the size-fractionated particulate samples is presented in Figure 11-1. Analysis of nitric acid digestates was used to represent the highest degree of surface availability for metals not bound in the alumina-silica fly ash matrix. A simulated gastric fluid and an acetic acid buffer solution were selected to extract metals representative of ingestion and ground water leaching mechanisms, respectively. ICP-MS was selected as the analytical technique over atomic

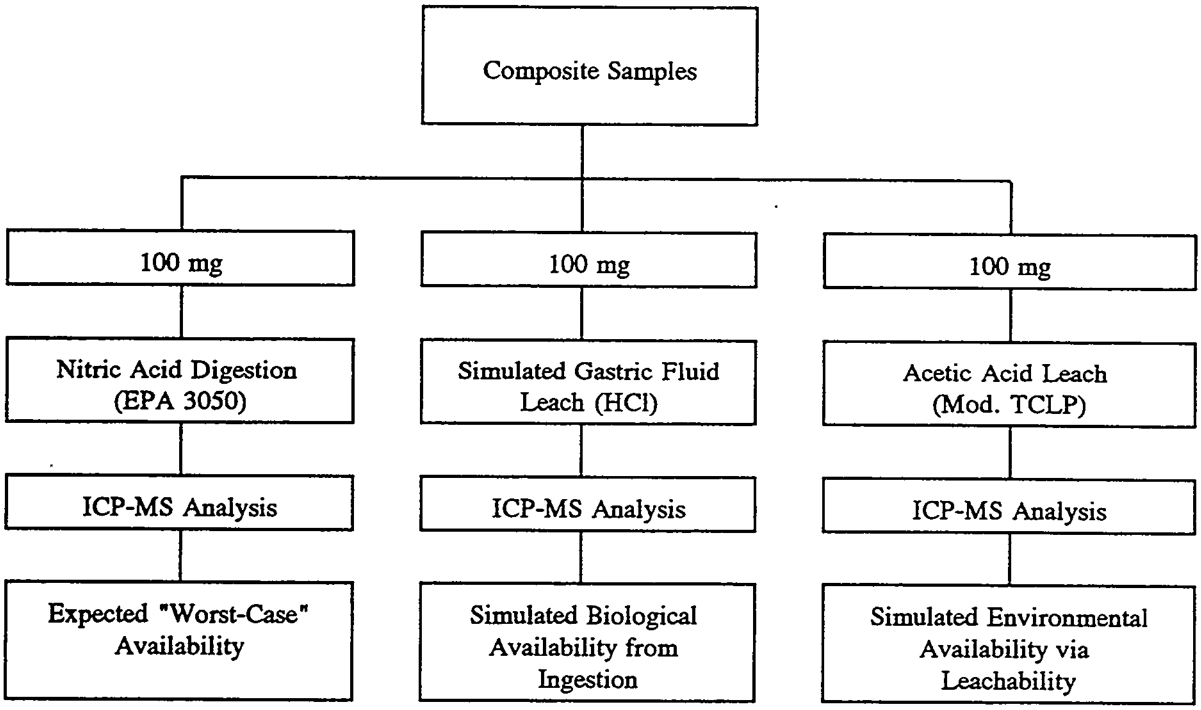

Figure 11-1
Gas Particulate Sample Preparation and Analysis Plan for Extractable Metals

emission and graphite furnace-atomic absorption spectrophotometry since these spectrophotometric techniques failed to provide the sensitivity required to accurately detect the target elements in the low concentration ranges expected.

Total Composition. Total composition analyses were performed on both the size-fractionated particulate samples, and on the filtered particulate matter collected with the multi-metals sampling train. Reported sample results were generated by ICP-AES and GFAA analyses in most cases; ICP-MS results were selected where elemental concentrations were below ICP-AES and GFAA detection limits. High background corrections, attributed to the inadvertent use of glass-fiber filters in some of the multi-metals trains invalidated many trace element results.

Therefore, the total composition of the fly ash collected from the ESP inlet and outlet ducts is represented by a composite of the size-fractionated particulate results. This substitution provided triplicate values for determining the average bulk composition for all trace elements. The resulting averages were biased universally low in these cases, so composition data from the multi-metals trains was not used. The exception is at the stack where two of the three filters used in the multi-metals train were quartz fiber, and no other metals composition data were available. The mass collected in each size fraction was determined relative to the sum, and then factored into the sum of the trace element concentrations. As a confirmation of the validity of this approach, the relative percent difference between the calculated values and the results obtained for fly ash collected from quartz-fiber filters was less than 30% for all elements except antimony, and selenium.

Nitric Acid Digestion. The strongest, most aggressive sample leaching technique performed on each particulate sample was a nitric acid digestion using EPA Method 3050. This procedure refluxes the sample in concentrated nitric acid and hydrogen peroxide. Metals present on the surface of the particle and those that may be loosely bound in the particle's matrix are digested. This technique does not totally digest the alumina-silica ash matrix and therefore may not account for some metals detected by total composition techniques.

All particulate samples were prepared by this method. Samples were digested, filtered through a 0.45 micron nitrocellulose membrane filter, and brought to a 100 mL final volume. Prior to analysis by ICP-MS, 1:20 dilutions were made to bring the sample into the linear range of the mass detector. To assess potential matrix interferences, one of the samples was selected as the source for a matrix spike. The sample selected was split to provide a sample for spiking, and the remaining sample was identified for duplicate analysis. The spike was prepared using a SPEX® multi-element ICP-MS calibration solution. Spike levels in the analyzed digestate were 50 ppb for all elements except molybdenum, which was not present in the calibration solution. This spiking level was based on previous results obtained from this procedure applied to standard reference fly ash samples.

Simulated Gastric Fluid Leach. Simulated gastric fluid is a solution of 85 mM hydrochloric acid, the enzyme pepsin, and sodium chloride. The pH of this solution is approximately 1.2. The leachability of metals in this matrix has a toxicological implication since some fly ash particles trapped in the mucous lining of the upper respiratory tract may be swallowed.

The dissolution of fly ash in gastric fluid represents a likely ingestion mechanism for toxic metals into the body.

Particulate samples were placed in a covered beaker with 10 mL of the gastric fluid solution and stirred mechanically for a minimum of 18 hours at room temperature. Using the same recovery procedure as the nitric acid digestates, the leachate was filtered and brought to a 100 mL final volume with DI water. Undiluted aliquots were analyzed by ICP-MS. In addition, a matrix spike was prepared, and the sample selected for spiking was identified for duplicate analysis. Gastric fluid matrix spikes were also prepared using the SPEX® ICP-MS calibrating solution and were prepared at 69 ppb for each of the target analytes except molybdenum. This spiking level was based on previous results obtained from this procedure applied to standard reference fly ash samples.

Because chloride ions pose adverse matrix effects for a number of the target elements analyzed by ICP-MS, calibration standards were prepared from the gastric fluid matrix to provide calibration curves with the same potential bias present in the samples. Arsenic is one of the key elements that is susceptible to mass detection interferences. Argon and chlorine, with atomic weights of 39.95 and 35.45, respectively, tend to form the polyatomic $ArCl^+$ ion with a mass of 75.4 amu. The high chloride levels in the gastric fluid, coupled with argon plasma source, generate a signal from $ArCl^+$ that can overwhelm the arsenic signal at 74.9 amu.

Acetic Acid Leach. The weakest of the three leaching solutions is an acetic acid solution prepared according to the EPA's Toxicity Characteristic Leaching Procedure[3] (TCLP). The TCLP is the regulatory standard procedure used to determine the hazardous nature of solid wastes. The protocol requires leaching of the solid waste in a buffered acetic acid solution that is maintained at a pH of 4.93 throughout the test. The metal concentrations determined in the acetic acid leachate are compared to regulatory standards to determine whether the material is classified as hazardous or nonhazardous.

The TCLP is designed for leaching sample quantities much larger than 100 mg, and to scale down the volumes specified in the method to accommodate the small quantity of particulate sample available was impracticable. Alternatively, 100 mg particulate samples were placed in a covered beaker with 10 mL of the buffered acetic acid solution (pH 4.93) and stirred for a minimum of 18 hours at room temperature. During this time, no additional pH adjustments were made to the acetic acid solution. Sample recovery and spiking were performed in the same manner as the gastric fluid leaching. The digestate was filtered and diluted to a 100 mL final volume before analysis by ICP-MS, and the same matrix spike and duplicate analysis scheme was used. The 69 ppb spiking level was also based on previous results obtained from this procedure when applied to standard reference fly ash samples.

Data Analysis

ESP Fly Ash

The extractability of metals from the surface of fly ash and flue gas particulate matter relates to a combination of factors. Metal solubility, particle surface area, surface concentration, or other matrix effects can influence the leachability of metals from particles. Increasing extractability was generally observed along the flue gas path, and the relationship between surface area, particle size, and surface concentration is considered influential.

For example, the analytical results for the various fly ash samples collected around the ESP all indicate differences in metal concentration as a function of particle size. Specifically, that enrichment of many trace elements increases as particle size decreases. This is evident from the evaluation of size-fractionated particulate samples collected from the ESP inlet and outlet flue gas (Section 8.0). An analysis of the fly ash collected from the first and second ESP fields also indicates this relationship between increasing trace element concentration and decreasing particle size. Trace element enrichment was more prominent in particles collected from the second (downstream) ESP field where the mean particle diameter was <10 microns, compared to 30 microns in the first field.

Since the samples collected for extraction were filtered, and not size-fractionated, the mean particle diameter of the samples is an important consideration. It is reasonable to expect higher extractable concentrations at the ESP outlet compared to the inlet, based solely on the reduction in the mean particle diameter across the ESP. The increased surface area associated with an equivalent sample mass exposes more material to the leaching solutions. Barium and vanadium are two elements whose total fly ash concentrations remained relatively constant across the ESP. But due to the smaller mean particle diameter of the ESP outlet sample, the extractable percentage by nitric acid digestion jumped from 39-59% for barium and from 35-61% for vanadium.

All of the remaining trace elements had higher bulk concentrations in the ESP outlet samples when compared to the ESP inlet. In this case, the increase in concentration and surface area exposure should produce an increase in the extractable percentage. Except for antimony, manganese, molybdenum, and mercury, this was true for all of the trace elements. Arsenic and selenium, when detected, showed little change. Tables 11-1 and 11-2 present the extractable metal concentrations of the ESP inlet and outlet fly ash, respectively. The total trace element concentration derived from size-fractionated particulate results is also presented along with the extractable percentage under each leaching condition.

Surface availability may be estimated from the extractable percentages between elements in samples from the same stream. Elements exhibiting the highest degree of extractability are likely to be surface oriented, unbound in the particle matrix, or in a form readily dissolved by the leaching agent. However, an analytical bias in the results for any given element may also manifest itself as high (or low) extractability.

Table 11-1
Extractable Composition of ESP Inlet Gas Particulate Matter

Trace Elements	Total Composition	Nitric Acid Digestion (EPA SW 3050)		Simulated Gastric Fluid Leach		Acetic Acid Leach (TCLP)	
	(μg/g)	(μg/g)	(% Extracted)	(μg/g)	(% Extracted)	(μg/g)	(% Extracted)
Antimony	3.18	2.68	84.3	0.709	22.3	0.798	25.1
Arsenic	44.8	42.6	95.1	<0.678	<1.5	1.02	2.3
Barium	560	220	39.2	103	18.4	48.1	8.6
Beryllium	11.2	4.11	36.7	1.14	10.2	0.322	2.9
Cadmium	3.45	2.22	64.5	1.82	52.9	1.65	47.9
Chromium	197	29.0	14.7	27.5	14.0	7.37	3.7
Cobalt	36.5	5.03	13.8	1.80	4.9	1.48	4.0
Copper	108	32.1	29.8	9.96	9.2	10.9	10.2
Lead	76.4	39.3	51.4	9.37	12.3	0.205	0.3
Manganese	236	120	51.1	60.0	25.5	51.4	21.8
Molybdenum	28.5	42.9	151	29.3	103	1.45	5.1
Nickel	134	45.1	33.8	10.3	7.7	8.64	6.5
Selenium	8.51	<23.3	<274	<0.884	<10.4	0.221	2.6
Vanadium	421	146	34.6	<0.359	<0.1	1.46	0.3

Table 11-2
Extractable Composition of ESP Outlet Gas Particulate Matter

Trace Elements	Total Composition	Nitric Acid Digestion (EPA SW 3050)		Simulated Gastric Fluid Leach		Acetic Acid Leach (TCLP)	
	(μg/g)	(μg/g)	(% Extracted)	(μg/g)	(% Extracted)	(μg/g)	(% Extracted)
Antimony	6.79	3.21	47.4	0.954	14.1	0.875	12.9
Arsenic	103	98.4	95.4	<0.660	<0.6	3.38	3.3
Barium	540	318	58.8	125	23.2	44.1	8.2
Beryllium	13.7	5.43	39.6	2.72	19.8	0.981	7.1
Cadmium	9.23	9.79	106	5.86	63.5	9.57	104
Chromium	248	64.3	25.9	54.3	21.8	19.5	7.8
Cobalt	44.3	16.9	38.3	5.47	12.3	6.02	13.6
Copper	152	98.5	64.9	33.5	22.1	17.9	11.8
Lead	141	116	82.3	32.9	23.4	1.50	1.1
Manganese	497	165	33.1	46.2	9.3	39.3	7.9
Molybdenum	69.1	72.2	105	61.4	88.9	4.43	6.4
Nickel	177	83.8	47.5	38.4	21.7	22.7	12.8
Selenium	101	<23.3	<23.1	18.1	18.0	4.07	4.0
Vanadium	448	272	60.7	122	27.3	4.68	1.0

Table 11-3 ranks the overall extractability of the target elements from fly ash in order from highest to lowest using the percent extractable results from all three leaching techniques. Elements with matrix spike recovery results outside the data quality objective range of 75-125% are identified, and as stated previously, may bias the relative extractability information.

To assess the accuracy of the extractable concentration data, matrix spikes were performed for each leachate matrix as indicators of analytical bias. A complete table of matrix spike recoveries for each of the leachate matrices is presented in Table D-2 of Appendix D. Based on the poor matrix spike and blank spike recoveries, mercury results were invalidated. QC sample results for arsenic in the gastric fluid leachates illustrate the difficulty of arsenic analysis by ICP-MS in a high chloride matrix. Molybdenum and antimony were not included in the spiking solution. Consequently, no spike recovery information is available for qualifying the accuracy of their results.

In addition to matrix spike recovery results, additional factors influencing the extractability data include bias in the bulk composition results. For example, the extractable concentrations of molybdenum reported for nitric acid and gastric fluid is above 100 percent. This element may indeed be 100% extractable from the particle surfaces or there could be an analytical bias in the total composition.

Stack Gas Particulate Matter

Particulate emissions from the FGD system were also characterized using extractability percentages to relate particle size, surface area, and surface concentration of the target elements. However, there are additional mechanisms to consider with the potential for scrubber mist carryover, (i.e., salts) and the leachability of the gas-borne particulate matter through the wet FGD system. With an average FGD slurry pH of 4.5, the JBR provides a mechanism for leaching some elements from the incoming fly ash. A shift in mean particle diameter is also observed as the larger sized particles are trapped in the scrubber.

Table 11-4 presents the extractable metal concentrations, the trace element concentration derived from multi-metals train results for test Runs 2 and 3 (quartz filters used), and the extractable percentage under each leaching condition. Only the results from extractable metals test Run 2 were selected for reporting the stack concentrations since glass-fiber filters were inadvertently used to collect particulate matter from the stack gas during test Runs 1 and 3. Data for the omitted test runs are reported in the Appendix.

Several metals were detected in the leachates at concentrations higher than the equivalent total composition value. Metals extracted by nitric acid digestion at percentages greater than 120% of the bulk composition include: beryllium, vanadium, lead, copper, arsenic, barium, and cadmium. Extractable percentages greater than 120% by gastric fluid leaching are reported for lead and beryllium. Clearly a bias exists in the analysis of either the stack gas particulate matter collected by the multi-metals train, the single Run 2 sample for extractable metals, or both.

Table 11-3
Extractability of Elements in Fly Ash[a]

Extractability (Highest - Lowest)	Average % Extractable	Average Matrix Spike Recovery	Spike Recovery Range
Molybdenum[c]	76%	Not Available[c]	Not Available[c]
Cadmium	73%	96.2%	107% - 88%
Antimony[c]	34%	Not Available[c]	Not Available[c]
Arsenic[b]	33%	80.5%	123% - 0%[b]
Selenium[b]	30%	117%	138%[b] - 84%
Lead	29%	87.7%	97% - 83%
Barium	26%	89.7%	94% - 85%
Manganese[b]	25%	88.8%	108% - 71%[b]
Copper	25%	98.8%	105% - 92%
Nickel	22%	95.3%	103% - 81%
Beryllium	19%	93.1%	108% - 79%
Vanadium[b]	19%	71.0%[b]	109% - 0%[b]
Chromium	15%	97.6%	106% - 88%
Cobalt	15%	97.7%	100% - 92%

[a] Results consider average extractability of elements from fly ash samples collected from the flue gas at the inlet and outlet of the ESP.

[b] Indicates that the spike recovery result obtained is outside the data quality objective range of 75-125 percent. The ranking of these elements may be biased by analytical results indicating higher or lower extractable percentages.

[c] Antimony and molybdenum were not present in the SPEX® ICP-MS calibration solution used to prepare matrix spikes. No spike recovery information is available to determine the relative accuracy of these results. Consequently, the extractable percentages for these elements could be affected by analytical bias.

Table 11-4
Extractable Composition of Stack Gas Particulate Matter

Trace Elements	Total Composition	Nitric Acid Digestion (EPA SW 3050)		Simulated Gastric Fluid Leach		Acetic Acid Leach (TCLP)	
	(μg/g)	(μg/g)	(% Extracted)	(μg/g)	(% Extracted)	(μg/g)	(% Extracted)
Antimony	31.5	5.78	18.4	3.37	10.7	<0.034	<0.1
Arsenic	81.1	164	202	<2.46	<3.0	<0.497	<0.6
Barium	214	354	165	214	100	17.2	8.0
Beryllium	2.94	10.2	349	4.20	143	2.91	98.9
Cadmium	41.4	67.0	162	12.4	29.9	5.92	14.3
Chromium	329	43.8	13.3	84.7	25.7	36.4	11.1
Cobalt	18.1	<0.899	<5.0	10.9	60.4	7.47	41.3
Copper	55.8	124	222	51.3	91.9	63.8	114
Lead	35.7	90.8	254	65.8	184	20.0	56.1
Manganese	488	328	67.2	349	71.5	470	96.3
Molybdenum	100	51.4	51.4	48.6	48.6	3.45	3.5
Nickel	2509	392	15.6	169	6.7	66.2	2.6
Selenium	899	<86.9	<9.7	140	15.6	61.2	6.8
Vanadium	122	385	315	<1.30	<1.1	<0.185	<0.2

Results for matrix spikes performed on the extractable metals sample collected at the ESP inlet and the multi-metals train samples are presented in Table D-2 of Appendix D. Since no QC activities were performed specific to the extractable metals Run 2 sample, data quality can only be estimated from relevant matrix and analytical spike data. In addition, the selection of only one sample result for comparison provides a high degree of uncertainty with these results.

Elements that were found in the stack gas particulate matter at concentrations greater than the ESP outlet (FGD inlet) gas are: antimony, cadmium, chromium, molybdenum, nickel, and selenium. Lower concentrations are noted for arsenic, barium, beryllium, cobalt, copper, lead, and vanadium. The concentration of manganese remained relatively constant across the FGD system.

The reduction in elemental concentrations, in spite of the reduction in mean particle diameter, across the JBR suggests that some elements may be leached from the fly ash by the FGD slurry. Some dilution of the fly ash by FGD solids low in certain trace elements may also be occurring; however, a comparison between calcium concentrations in the gas particulate-phase samples across the JBR system revealed only a slight, and statistically insignificant, increase in calcium concentration.

A comparison of trace metal concentrations between limestone slurry and JBR slurry filtrates suggests that the slurry is leaching trace elements from the fly ash. Enrichment is observed (in order of highest to lowest enrichment) for cadmium, lead, manganese, copper, selenium, cobalt, arsenic, nickel, vanadium, beryllium, and chromium at concentration factors much greater than the 6 cycles of concentration observed for soluble silica. In addition to these elements enriched in the aqueous phase, molybdenum, selenium, vanadium, and arsenic are enriched in the JBR slurry's solid phase.

This concentration mechanism plays an important part in the study of extractable metals in gas particulate matter downstream of wet scrubbing systems. As a result, particle surface characterizations based on extractability data may not be feasible without a more thorough understanding of the enrichment and carryover mechanisms taking place in the scrubber system.

References

1. 40 CFR 60, Appendix A. *Test Methods.* "Method 17: Determination of Particulate Emissions from Stationary Sources (In-Stack Filtration Method)."

2. 40 CFR 60, Appendix A. *Test Methods.* "Method 5: Determination of Particulate Emissions from Stationary Sources."

3. 55 FR 26986 (Friday, June 29, 1990), "Toxicity Characteristic Leaching Procedure (Method 1311)."

APPENDIX A: QUALITY ASSURANCE AUDITS

The purpose of a quality assurance audit is to provide an objective, independent assessment of a sampling or measurement effort. It ensures that the sampling procedures, data generating, data gathering, and measurement activities produce reliable and useful results. Sometimes inadequacies are identified in the sampling/measurement system and/or the quality control program. In such cases, audits provide the mechanism for implementing corrective action.

A technical systems audit (TSA) is an on-site, qualitative review of the various aspects of a total sampling and/or analytical system. It is an assessment of overall effectiveness and represents an objective evaluation of a set of interactive systems with respect to strengths, deficiencies, and potential areas of concern. The audit consists of observations and documentation of all aspects of the measurement effort.

A performance audit is an independent check to evaluate the data produced by a measurement system. Audit standards and test equipment which are traceable to acceptable reference standards are used to assess the performance of each analytical method and/or measurement device (performance audit). Performance audits are designed to provide a quantitative, point-in-time evaluation of the data quality of the sampling and analytical systems being tested. This is accomplished by addressing specific parts of the overall system. Each performance audit addresses two general measurement categories of a project:

- Chemical analysis of samples; and

- Physical measurements supporting the sampling effort.

Audit activities consist of challenging the various measurement systems with standards and test equipment traceable to accepted reference standards. Laboratories conducting the analytical work on a program are given performance audit samples prepared by spiking representative sample matrices with target analytes at representative concentration levels. Results for these audit samples are tabulated and considered in evaluating the analytical performance and data reporting protocols for each laboratory.

For this program, technical system audits and performance audits were conducted of each of the DOE contractors by Research Triangle Institute (RTI) under contract to EPA. For the audits of the Radian activities, reports were prepared and subsequently distributed to Radian through DOE detailing the results of the audits. Copies of the RTI audit reports are presented as attachments to this appendix. The following subsections present the Radian response to RTI's findings.

Technical Systems Audit Results

A technical systems audit was conducted of the sampling and on-site analytical activities for this program on June 23-25, 1993. This audit was conducted by J.B. Flanagan and C.O. Whitaker of RTI. Four findings were discussed in the RTI audit report. Each of these findings and RTI recommendations are discussed in the following paragraphs.

Finding 1

Basis due to long sampling lines from the calibration tanks to the probes and nonlinearity of the continuous monitor (CEM) system may go undetected due to infrequent multi-point calibrations. The CEM system at Plant Yates was not a designated part of the Radian effort for the DOE program and was not a negotiated activity between DOE and Georgia Power. Therefore, Radian has no control over and may not initiate any corrective actions related to, the operation of the CEM at Plant Yates.

Finding 2

Aldehyde measurements were performed in accordance with the method; however, acetone (a possible contaminant) was present in the mobile laboratory as a wash bottle under the hood. One or more of the field blanks for the aldehyde sampling trains showed varying concentrations of acetaldehyde and formaldehyde. However, these analytes were not found in the reagent blanks stored in the mobile laboratory. It is not possible with the data available to rule out possible contamination due to the wash bottle of acetone. The concentrations found in the blanks should be considered in the use of the sample data. This precaution was noted in the project QA/QC summary (see Appendix D).

Finding 3

All plant and sampling times are recorded in Central Daylight Savings Time instead of Eastern Daylight Savings Time. Radian has worked on several other Georgia Power projects and is familiar with their timekeeping procedures. In addition, since the field crew was from one of Radian's offices located in the Central Time Zone, the use of CDT was probably less confusing than working on EDT.

Finding 4

Sampling data are hand-entered from field sheets into a portable computer each day, making occasional typographical errors virtually unavoidable. The normal Radian practice is to compare the computer output with the original data sheets to ensure that the information has been input correctly. This is generally done once the field crew has returned to the office and the summary report of field activities is prepared. In addition, the Radian QA coordinator or his/her designee checks a percentage of the data sheets, logbooks, and calculations.

In addition to the technical systems audit, a number of performance evaluation audits were performed during the on-site effort. The greater part of the performance audit was directed toward the off-site analyses and a lesser part to the on-site activities. The results of the off-site performance audit samples are discussed in the next section. The results of the on-site performance audit are discussed in the following paragraphs.

Orsat Determinations

A duplicate analysis of oxygen was performed using a test gas supplied by RTI. The results of the analysis of test gas BLM002689 was 9.0% oxygen which calculates out to a 97.8% recovery as compared to the theoretical concentration of 9.2 percent.

Source Sampling Consoles

An audit of the dry gas meters in four source sampling consoles was performed by RTI using a standard orifice. Audit results calculated as relative percent difference between the dry gas volume measurement and the calculated volume based on the RTI orifice were within the ±10% acceptance criteria for three of the four meters tested. The result for the fourth meter (-11.7%) was just slightly below the criteria. The auditor noted that the audit data set for this meter did not include a meter run stop time. It is not known if a more exact run time would have resulted in this measurement being within the criteria.

Continuous Emissions Monitors

Audit of the continuous emissions monitors was not an negotiated activity between Georgia Power and DOE for this program. Therefore, Plant Yates would not permit RTI to audit the CEM. Any change in the frequency of the calibration approach would have to be decided between DOE and Georgia Power (The yearly calibration is actually a yearly certification or performance audit).

In the RTI audit report five recommendations are discussed. Since the majority of these recommendations were not discussed at the audit wrap-up meeting conducted at Plant Yates, limited corrective action was initiated. A summary of the RTI recommendations and the Radian corrective actions are discussed in the following paragraphs:

Recommendation 1

Due to the unusually large differences seen between the RTI standard orifice and the sampling consoles used for source testing, it is recommended that the average of the pre- and post- test calibrations be used in the emission estimates. Only one of the consoles audited by RTI was outside the acceptance criteria given. The theoretical value for this audit run is not certain because the meter run stop time was not recorded. Therefore, it is not known if the result for this console was actually outside the acceptance criteria. A QA check of the post-test calibration for the consoles used on the project showed that the difference between the pre-test and post-test calibrations was less than 5% as required by the method (RPD-1.38% ±1.08, Range 0.1%-3.47% per Radian QA coordinator).

Recommendation 2

Mass flow rates for solids such as bottom ash and ESP ash are calculated based on coal feed rates and percentage ash in the coal obtained by proximate/ultimate analysis. One or more independent, direct methods of measuring or estimating the amount of ash produced should be attempted. The ESP collected ash flow rate was determined using the measured particulate loadings at the ESP inlet and outlet and the measured gas flow rate, not the coal feed rate and coal ash concentration. The bottom ash was calculated using the ESP inlet particulate loadings and coal feed rate and ash concentration. Radian considered obtaining representative bottom ash and ESP collected ash flow rates using the method described by RTI. However, the level of effort required, particularly for the ESP collected ash flow rate would have required additional sampling personnel and, given the physical design of the ash sluice system, additional information gained in this manner would also have a very large degree of uncertainty as to its accuracy.

Recommendation 3

Because RTI auditors were not allowed to take any completed data sheets off-site, a data audit should be conducted in which raw data sheets, computer-logged data, logbooks, validation procedures, and calculations are examined. Data quality audits of the raw data, logbooks, calculations, and computerized data are checked and counter checked by various project personnel (including the Radian QA coordinator) throughout the progress of the project. The overall project is then peer- reviewed by senior engineers and scientists at least twice prior to the final reporting process.

Recommendation 4

CEMs at Plant Yates are not scheduled for multi-point calibration until the fall of 1993 which will result in a one-year interval since the last multi-point calibration. The interval between multi-point calibrations of the CEM should be changed from yearly to every six months. This recommendation is outside of the scope of the present project and is out of the control of Radian.

Recommendation 5

The major elements for mass balance determinations should be discussed and finalized between DOE and Radian. Elements for the mass balance determinations were finalized between DOE and Radian and are presented in Section 6 of this Document.

Performance Audit Results

At the time of the technical systems audit conducted by RTI in June 1993, a series of performance audit samples were prepared and presented to the Radian sampling team to be submitted to the various analytical laboratories along with the investigative samples. The audit samples were prepared by spiking the impinger solutions or other analytical matrices provided to the auditors by Radian.

VOST

Two sets of Tenax cartridges were spiked with 18 compounds. These were analyzed for 16 of the 18 compounds by Radian's subcontractor, Air Toxics, Limited. In the RTI audit report, the results for these analyses were compared to the wrong set of recovery objectives. Tables A-1 and A-2 show the results and the recovery objectives for volatile organics as presented in Table 9-4 (page C9-9) of the project QAPP. The QC objectives were met for 10 of the 16 analytes in sample Y194 and 9 of the 16 analytes in sample Y195. Of the analytes with recoveries outside the QC objectives, toluene, methylene chloride, 1,1,1-trichloroethane, trichlorofluoromethane, benzene, chloroform, and carbon tetrachloride were recovered high in one or more of the samples and chlorobenzene was recovered low in one sample. A portion of the methylene chloride recovery may be due to contamination, since this analyte was found in varying concentrations in most of the field and laboratory blanks analyzed with the samples. The high toluene recoveries were also attributed to contamination in the RTI audit report. In this case, the contamination appears to be in the audit cylinder, since this analyte was not found in any of the field or laboratory blanks and the concentration in Y195 is approximately twice the concentration in Y194. This concentration ratio matches the relationship for the RTI theoretical concentrations for other analytes in the two samples.

Semivolatile Organics

Two XAD-2 modules, a train rinse, and a probe rinse were spiked with 16 analytes. Each module was combined with a rinse and reported as a combined sample. The analytical results for the 16 spiked compounds were within the project objectives for sample Y173-177 and 14 of the 16 spiked compounds were within the QC objectives in sample Y178-182. Anthracene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene, and benzo(g,h,i)perylene results were outside the QC objectives. These compounds were spiked at or near the approved detection limits stated in the project QAPP.

Aldehydes

Two DNPH impinger solutions were spiked with formaldehyde. The recovery for this analyte showed recoveries above the stated project QC objectives. RTI attributed these apparent enhanced recoveries to possible contamination. Formaldehyde was found in several of the field blanks and at the detection limit in one laboratory blank but was not found in the reagent blanks. Laboratory control samples and matrix spiked samples showed good recoveries for both formaldehyde and acetaldehyde.

Table A-1
Analysis of Vost Sample ID Y194 by Air Toxics Limited

Analyte	Detection Limit (ng)	Theoretical Concentration (ng)	Analyzed Concentration (ng)	% Recovery	QC Objectives % Rec.	QC Objectives Met?
Benzene	10	63.73	74	116	37-151	yes
Chlorobenzene	10	177.43	53	30	37-160	low
Ethylbenzene	10	153.86	120	78	37-162	yes
Toluene	10	151.68	2300	1520	47-150	high
o-Xylene	10	159.30	71	45	NS	NA
Bromomethane	10	125.33	130	104	D-242	yes
1,3-Butadiene	NA	25.94	NA	-	-	NA
Chloroform	10	87.60	110	126	51-138	yes
Carbon tetrachloride	10	123.28	140	114	70-140	yes
1,2-Dichloroethane	10	74.04	53	72	49-155	yes
1,2-Dibromoethane	NA	300.37	NA	-	-	NA
1,2-Dichloropropane	10	192.00	160	83	D-210	yes
Methylene chloride	10	112.98	5700	5040	D-221	high
Tetrachloroethylene	10	141.40	120	85	46-157	yes
Trichloroethylene	10	103.69	120	116	71-157	yes
1,1,1-Trichloroethane	10	148.77	230	155	52-150	high
Trichlorofluoromethane	10	217.11	470	216	17-181	high
Vinyl chloride	10	40.10	48	120	D-251	yes

Table A-2
Analysis of Vost Sample ID Y195 by Air Toxics Limited

Analyte	Detection Limit (ng)	Theoretical Concentration (ng)	Analyzed Concentration (ng)	% Recovery	QC Objectives % Rec.	QC Objectives Met?
Benzene	10	125.29	190	152	37-151	high
Chlorobenzene	10	348.80	170	49	37-160	yes
Ethylbenzene	10	302.47	420	139	37-162	yes
Toluene	10	298.18	4000	1340	47-150	high
o-Xylene	10	313.17	290	93	NS	-
Bromomethane	10	246.38	180	73	D-242	yes
1,3-Butadiene	NA	51.00	NA	-	-	NA
Chloroform	10	172.22	250	145	51-138	high
Carbon tetrachloride	10	242.36	360	148	70-140	high
1,2-Dichloroethane	10	145.55	150	103	49-155	yes
1,2-Dibromoethane	NA	590.50	NA	-	-	NA
1,2-Dichloropropane	10	377.45	410	109	D-210	yes
Methylene chloride	10	222.11	5800	2610	D-221	high
Tetrachloroethylene	10	277.98	350	126	46-157	yes
Trichloroethylene	10	203.84	320	157	71-157	yes
1,1,1-Trichloroethane	10	292.47	550	188	52-150	high
Trichlorofluoromethane	10	426.22	660	155	17-181	yes
Vinyl chloride	10	78.83	98	124	D-251	yes

NA = Not analyzed.

NS = Not specified.

RTI analyzed the spike solution (about two months later) and found reduced recoveries based on the nominal concentration. It appears that the true concentration of the spike solution is not known. Formaldehyde standards prepared from the commercially available 37% solutions may vary since these reagents may vary in actual concentration from 36-41 percent. Standards prepared as nominal concentrations can be analyzed by a titration procedure to obtain a known concentration for a standard. It is not known if this procedure was used by RTI to assign a theoretical concentration for the spike solution.

Metals

Performance audit samples were prepared by RTI for the filter, the nitric acid-peroxide impingers, and the permanganate impingers of the multi-metals sampling train. Arsenic, cadmium, lead, and selenium were recovered within the QC objectives in the nitric acid/peroxide impinger solutions. However, mercury showed a slightly high recovery in this solution. Metal recoveries for the two spikes onto blank filters showed good recoveries except for one arsenic spike with a high recovery and one cadmium, selenium, and mercury spike with slightly low recoveries on the other filter. Mercury spiked into the two permanganate impinger solutions showed low recoveries (21-40%). The performance audit sample prepared by the Radian QA Coordinator also showed low recovery (33%) for the permanganate solution sample.

Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, Pennsylvania 15236-0940

November 10, 1993

Barbara J. Hayes
Radian Corporation
8501 Mo-Pac Blvd.
P.O. Box 201088
Austin, TX 78720-1088

Dear Barbara:

Enclosed are clean copies of the Field Sampling Report and the PE Sample Analysis information prepared by Research Triangle Institute. Please include these documents in the External Audit Section of the Draft Final Report to be submitted to the DOE on December 10, 1993. In addition, provide a response to RTI's finding in the Draft Final Report.

If you have any questions, please call me at (412) 892-4691.

Thomas D. Brown
Project Manager
Environmental Control Division

Enclosures

CC: Hollis Flora, Radian

RESEARCH TRIANGLE INSTITUTE

Center for Environmental Measurements and Quality Assurance

October 4, 1993

Mr. Tom Brown
PETC, U.S. Department of Energy
P.O. Box 10940, M.S. 922-206
Pittsburgh, PA 15236

Subject: Radian PE sample analysis during the Yates Plant Audit

Dear Tom:

Enclosed are the analysis results for 10 sets of performance evaluation (PE) samples given to Radian Corporation during the audit of the Yates plant. Of particular concern are the mercury and the formaldehyde analyses.

After encountering a serious problem with the aldehyde analysis, we recalculated the PE sample concentrations and analyzed the samples in our laboratory. In the analytical procedure, there are still some undetermined factors such as the percent conversion of aldehyde into the DNPH-derivatives. Even though the molar ratios of DNPH to aldehyde were sufficiently high to drive the conversion reaction to completion, the aldehyde analysis results are lower than expected. The further laboratory work may resolve this issue.

Volatiles

RTI spiked two sets of Tenax cartridges in a VOST train with 18 compounds. The cartridges were analyzed by Radian's subcontractor, Air Toxics, Limited. The laboratory analyzed for 16 of the 18 compounds spiked into the cartridges. Of the compounds quantitated, 10 of 16 were recovered within the data quality objectives (DQOs) set by Radian for sample Y194, and 9 of 16 were recovered within the DQOs for sample Y195. Of the compounds particularly relevant to this project (benzene, toluene, ethylbenzene, and o-xylene), recoveries were mixed. Benzene was recovered well within range on sample Y194, but slightly out of range on sample Y195. Toluene was recovered completely out of range on both samples due to apparent contamination. Ethylbenzene was recovered within range on both samples. O-xylene was recovered out of range on sample Y194, but within range on sample Y195.

Semivolatiles

RTI spiked two XAD-2 modules, a train rinse, and a probe rinse with 16 PAHs in solution. Each module was combined with a rinse and reported by Radian as a combined sample. Radian performed satisfactorily on 28 of the 32 analyses. One undetected analyte was spiked at below the reported detection limit. This occurred because the detection limits reported were much higher than the 1 ng/m^3 required by DOE for the project.

Metals on Filters

Several metals were spiked onto two filters of the M-29 trains to simulate metals in the particulate catch. Radian recovered 6 of the 10 metals concentrations within the limits of their DQOs.

Metals in Impinger Solutions (HNO_3/H_2O_2)

Several metals were spiked into the first impinger of the metals train. Radian recovered eight of the nine metals within the limits of their DQOs.

Metals in Impinger Solutions ($KMnO_4$)

Mercury was spiked into two acidic $KMnO_4$ solutions. Neither was recovered in the range of their DQOs (75 to 125%).

Formaldehyde in Impinger Solutions (DNPH)

RTI spiked two DNPH impinger solutions with a solution containing a nominal concentration of 0.4068 µg/µl. Radian's recoveries calculated based on this concentration are higher indicating possible contamination. RTI has analyzed the spiking solution and our recovery based on the nominal value is 67.6% (average concentration of 0.275 µg/µl). RTI is continuing verification analyses on the spiking solution.

If I can be of further assistance, please call me at 541-5919.

Sincerely,

Shri Kulkarni

Shri Kulkarni, Ph.D.
Manager, Quality Assurance and
Technology Assessment Department

SVK:dmh

cc: S.J. Wasson
J. McSorley

File: 5960-193/4805
91A-04

METALS IN IMPINGER SOLUTIONS (HNO_3/H_2O_2)

SAMPLE ID: Y276

METAL	RTI AMOUNT (µg)	RADIAN AMOUNT (µg)	PERCENT RECOVERY	RECOVERY[1] DQO (%)	DQO MET
As	50	52.10	104.2	75-125	Yes
Cd	30	37.00	123.3	75-125	Yes
Pb	20	19.79	98.9	75-125	Yes
Se	40	41.60	104.0	75-125	Yes
Hg	10	12.68	126.8	75-125	No

METALS IN IMPINGER SOLUTIONS (HNO_3/H_2O_2)

SAMPLE ID: Y279

METAL	RTI AMOUNT (µg)	RADIAN AMOUNT (µg)	PERCENT RECOVERY	RECOVERY[1] DQO (%)	DQO MET
As	15	15.03	100.2	75-125	Yes
Cd	60	68.26	113.8	75-125	Yes
Pb	40	42.34	105.9	75-125	Yes
Se	80	90.72	113.4	72-125	Yes

[1] These values are taken from Radian's QA plan (page C9-7).

METALS ON FILTERS

SAMPLE ID: Y278, filter 966

METAL	RTI AMOUNT (µg)	RADIAN AMOUNT (µg)	PERCENT RECOVERY	RECOVERY[1] DQO (%)	DQO MET
As	40	84.4	211.0	75-125	No
Cd	10	9.59	95.9	75-125	Yes
Pb	15	15.3	102.0	75-125	Yes
Se	25	22.3	89.2	75-125	Yes
Hg	10	10	100.0	75-125	Yes

METALS ON FILTERS

SAMPLE ID: Y281, filter 974

METAL	RTI AMOUNT (µg)	RADIAN AMOUNT (µg)	PERCENT RECOVERY	RECOVERY[1] DQO (%)	DQO MET
As	25	27.9	111.6	75-125	Yes
Cd	15	10.6	70.7	75-125	No
Pb	25	25.3	101.2	75-125	Yes
Se	35	23.4	66.9	75-125	No
Hg	20	14.6	73.0	75-125	No

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[1] These values are taken from Radian's QA plan (page C9-7).

MERCURY IN IMPINGER SOLUTIONS (KMn04)

SAMPLE ID	RTI AMOUNT (µg)	RADIAN AMOUNT (µg)	PERCENT RECOVERY	RECOVERY[3] DQO (%)	DQO MET
Y277[1]	20	4.18	20.9	75-125	No
Y280[2]	50	19.75	39.5	75-125	No

FORMALDEHYDE IN IMPINGER SOLUTIONS (DNPH)

SAMPLE ID	RTI AMOUNT (µg)	RADIAN AMOUNT (µg)	PERCENT RECOVERY	RECOVERY[4] DQO (%)	DQO MET
Y187	24.4	76	311	50-150	No
Y188	34.2	90	263	50-150	No

[1] Also spiked with 30 µg Pb.
[2] Also spiked with 20 µg As.
[3] These values were taken from Radian's QA plan (page C9-7).
[4] These values were taken from Radian's QA plan (page C9-8).

SVOC RECOVERIES FROM XAD-2 MODULES

SAMPLE ID: Y178-182 (Combined)

ANALYTE	RTI VALUE (µg)	Radian VALUE (µg)	PERCENT RECOVERY	RECOVERY[1] DQO (%)	DQO MET
Naphthalene	10	9.98	99.8	21-133	Yes
Acenaphthylene	20	17.3	86.5	33-145	Yes
Acenaphthene	10	8.22	82.2	47-145	Yes
Fluorene	2	1.19	59.5	59-121	Yes
Phenanthrene	1	0.853	85.3	54-120	Yes
Anthracene	1	ND[2]	0.0	27-133	No
Fluoranthene	2	1.44	72.0	26-137	Yes
Pyrene	1	0.634	63.4	52-115	Yes
Chrysene	1	0.844	84.4	17-168	Yes
Benzo(a)anthracene	1	0.694	69.4	33-143	Yes
Benzo(b)fluoranthene	2	1.4	70.0	24-159	Yes
Benzo(k)fluoranthene	1	0.713	71.3	11-162	Yes
Benzo(a)pyrene	1	0.484	48.4	17-163	Yes
Indeno(1,2,3-cd)pyrene[3]	1	ND[2]	0.0	D-171	No
Dibenz(a,h)anthracene	2	ND[2]	0.0	D-227	No
Benzo(g,h,i)perylene	2	ND[2]	0.0	D-219	No
Other Compounds Reported					
Acetophenone	0	0.694	--	--	--
Benzoic Acid	0	14.2	--	--	--
Diethylphthalate	0	0.689	--	--	--

[1] Recovery DQOs (%) were taken from Radian's QA plan (Page C9-10).

[2] ND = not detected.

[3] This compound was spiked at a concentration below the reported detection limit of 1.33 µg.

SVOC RECOVERIES FROM XAD-2 MODULES

SAMPLE ID: Y173-177 (Combined)

ANALYTE	RTI VALUE (μg)	RADIAN VALUE (μg)	PERCENT RECOVERY	RECOVERY[1] DQO (%)	DQO MET
Naphthalene	35.0	30.1	86.0	21-133	Yes
Acenaphthylene	70.0	62.8	89.7	33-145	Yes
Acenaphthene	35.0	28.7	82.0	47-145	Yes
Fluorene	7.0	4.53	64.7	59-121	Yes
Phenanthrene	3.5	2.54	72.6	54-120	Yes
Anthracene	3.5	2.5	71.4	27-133	Yes
Fluoranthene	7.0	4.42	63.1	26-137	Yes
Pyrene	3.5	2.13	60.8	52-115	Yes
Chrysene	3.5	1.52	43.4	17-168	Yes
Benzo(a)anthracene	3.5	1.65	47.1	33-143	Yes
Benzo(b)fluoranthene	7.0	2.82	40.3	24-159	Yes
Benzo(k)fluoranthene	3.5	1.62	46.3	11-162	Yes
Benzo(a)pyrene	3.5	1.33	38.0	17-163	Yes
Indeno(1,2,3-cd)pyrene	3.5	1.33	38.0	D-171	Yes
Dibenz(a,h)anthracene	7.0	2.14	30.6	D-227	Yes
Benzo(g,h,i)perylene	7.0	2.19	31.3	D-219	Yes
Other Materials Recovered					
Benzoic Acid	0	60.3	--	--	--

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[1] Recovery DQOs (%) were taken from Radian's QA plan (page C9-10).

VOLATILE ORGANICS ON TENAX (VOST)

SAMPLE ID: Y194

COMPOUNDS	RTI AMOUNT (ng)	RADIAN AMOUNT (ng)	PERCENT RECOVERY	RECOVERY[1] DQO (%)	DQO MET
Vinyl Chloride	40.10	48	119.7	50-150	yes
Chloroform	87.60	110	125.6	50-150	yes
Carbon Tetrachloride	123.28	140	113.6	50-150	yes
Methylene Chloride	112.98	5700	5045.1	50-150	no
1,2 Dichloroethane	74.04	53	71.5	50-150	yes
Trichlorethylene	103.69	120	115.7	50-150	yes
Benzene	63.73	74	116.1	50-150	yes
Tetrachloroethylene	141.40	120	84.9	50-150	yes
1,3-Butadiene[1]	25.94	--	--	50-150	--
Bromomethane	125.33	130	103.7	50-150	yes
Trichlorofluoromethane	217.11	470	216.5	50-150	no
1,1,1-Trichloroethane	148.77	230	154.6	50-150	no
1,2-Dichloropropane	192.00	160	83.3	50-150	yes
1,2-Dibromoethane[2]	300.37	--	--	50-150	--
Toluene	151.68	2300	1516.4	50-150	no
Chlorobenzene	177.43	53	29.9	50-150	no
Ethylbenzene	153.86	120	78.0	50-150	yes
Ortho-Xylene	159.30	71	44.6	50-150	no
Other Compounds Reported					
Acetone	0	120	--	--	--

[1] Recovery DQOs (%) were taken from Radian's QA plan (page C9-10).

[2] This compound was not identified or analyzed by Radian's subcontractor, Air Toxics Limited.

VOLATILE ORGANICS ON TENAX (VOST)

SAMPLE ID: Y195

COMPOUNDS	RTI AMOUNT (ng)	RADIAN AMOUNT (ng)	PERCENT RECOVERY	RECOVERY[1] DQO (%)	DQO MET
Vinyl Chloride	78.83	98	124.3	50-150	yes
Chloroform	172.22	250	145.2	50-150	yes
Carbon Tetrachloride	242.36	360	148.5	50-150	yes
Methylene Chloride	222.11	5800	2611.3	50-150	no
1,2 Dichloroethane	145.55	150	103.1	50-150	yes
Trichlorethylene	203.84	320	157.0	50-150	no
Benzene	125.29	190	151.6	50-150	no
Tetrachloroethylene	277.98	350	125.9	50-150	yes
1,3-Butadiene[1]	51.00	--	--	50-150	--
Bromomethane	246.38	180	73.1	50-150	yes
Trichlorofluoromethane	426.82	660	154.6	50-150	no
1,1,1-Trichloroethane	292.47	550	188.1	50-150	no
1,2-Dichloropropane	377.45	410	108.6	50-150	yes
1,2-Dibromoethane[2]	590.50	--	--	50-150	--
Toluene	298.18	4000	1341.5	50-150	no
Chlorobenzene	348.80	170	48.7	50-150	no
Ethylbenzene	302.47	420	138.9	50-150	yes
Ortho-Xylene	313.17	290	92.6	50-150	yes
Other Compounds Reported					
Acetone	0	160	--	--	--

[1] Recovery DQOs (%) were taken from Radian's QA plan (page C9-10).

[2] This compound was not identified or analyzed by Radian's subcontractor, Air Toxics Limited.

RESEARCH TRIANGLE INSTITUTE

RTI/5960/193 - 04D

August 6, 1993

QA/QC AUDITS ON DOE UTILITY BOILER TEST PROGRAM

FIELD SAMPLING AUDIT REPORT

Site: Yates Station Unit 1, Newnan, GA

DOE Contractor: Radian Corporation

DOE Project Officer: Janice Murphy

Performed for

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Under EPA Contract No. 68D10009
Work Assignment No. I-193

Field Audit of:

Yates Station Unit 1
Georgia Power Company
Newnan, Georgia

Contractor: Radian Corporation
Dates: June 23-25, 1993
RTI Personnel: J. B. Flanagan and C. O. Whitaker

Introduction

The Yates Station Unit 1 is a bituminous coal-fired steam-electricity-generating unit with a net generating capacity of 105 megawatts. The station is located near Newnan, Georgia, and is owned and operated by Georgia Power Company. Unit 1 has a tangentially fired boiler manufactured by Combustion Engineering in 1949. During this test, the unit was fueled with 2.5% sulfur blend of Illinois No. 5 and Illinois No. 6 bituminous coals. The feed coal is a 50:50 blend mined from the "Arch Captain" and "Old Ben Franklin" mines.

The plant uses electrostatic precipitators for particulate control. Unit 1 currently controls sulfur dioxide (SO_2) using a Jet Bubbling Reactor (JBR) supplied under the CT-121 demonstration project. Sampling for the hazardous air pollutants (HAP) study is being carried out by Radian Corporation, which also operates the CT-121 demonstration project in cooperation with Georgia Power and DOE. The JBR process combines conventional limestone flue gas desulfurization (FGD) chemistry, forced oxidation, and gypsum crystallization in one reaction vessel. It is designed to operate in a medium-acid solution, where limestone is completely soluble and where the sulfite resulting from SO_2 absorption can be oxidized completely to sulfate. Attrition of gypsum crystals and problems of poor sludge quality and chemical scaling are also eliminated due to improvements of the second generation FGD process. The process is not specifically designed to destroy pollutants such as NO_2 or organics.

Findings

1. Finding: **Basis due to long sampling lines from the calibration tanks to the probes and nonlinearity of the continuous emission monitor (CEM) system may go undetected due to infrequent multipoint calibrations.** Line losses and multipoint calibrations are not normally measured and multipoint calibrations are not performed during the demonstration program; the next scheduled full calibration is scheduled for the changeover to Phase II of the demonstration program some time this fall. Daily zero-span checks are conducted for all CEMs.

Effect on Data: If there is loss of calibration gas in the 300 to 600 feet of tubing running from the cylinders to the probes, the span result will be biased. Sulfur dioxide is particularly sensitive to decomposition reactions on surfaces. The potential for nonlinearity is unknown in the absence of regularly scheduled multipoint calibrations.

2. Finding: **Aldehyde measurements were performed in accordance with the method; however, acetone, (a possible contaminant) was present in the mobile laboratory as a wash bottle under the hood.**

   Effect on Data: Any acetone that might be found in the samples would be suspect.

3. Finding: **All plant and sampling times are recorded in Central Daylight Savings Time instead of Eastern Daylight Savings Time.** The central power grid is controlled by Georgia Power's headquarters in Alabama, which is in the Central time zone. Yates plant personnel have adopted Central time to coordinate with the central operations. To avoid confusion, Radian also adopted Central time in conducting the HAP project.

   Effect on Data: Radian and plant personnel were all well-aware of this situation; however, special care should be taken to cross-check data to avoid confusion in sampling times during data validation.

4. Finding: **Sampling data are hand-entered from field sheets into a portable computer each day, making occasional typographical errors virtually unavoidable.**

   Effect on Data: Data validation procedures such as duplicate keying or 100% comparison with original sheets should be used to minimize these errors.

Observations

This section includes general observations for which no adverse effect on the data could necessarily be predicted, but which had the potential to differentiate results at this site from results at other sites.

1. Radian sent an analyst and a high performance liquid chromatography (HPLC) instrument to the site for Cr^{IV} measurements. Having the analyses performed on-site provides faster results: a 1/2- to 2-hour turnaround versus 24 hours or more when samples are sent back to an off-site laboratory. This conscientious effort to obtain more timely analyses of this unstable material should be taken into account when comparing Radian's results for Cr^{IV} with those from other contractors.

2. The "Nick Bloom" method for sampling vapor phase mercury differed from that of another contractor on this project in that differently sized charcoal tubes were used and different methods of analysis will be used. Radian also used a soda-ash tube in conjunction with the charcoal tube which was intended to allow discrimination between oxidation states of mercury. Results of different contractors may not be comparable if different implementations of this method are employed.

Activities

1. Meetings

Audit activities included three meetings between RTI, DOE, Georgia Power, and Radian personnel. An initial meeting was held on 6/22 and an exit meeting on 6/24. Additionally, there was a meeting on the afternoon of 6/22 in which the Georgia Power representatives expressed concerns about data security for the JBR project and misgivings about having "EPA representatives" on-site. Dr. Flanagan called Ms. Wasson, the RTI Project Leader, to inform her of this development immediately after this meeting. Dr. Kulkarni of RTI and Mr. Brown of DOE were contacted later the same day. No further concerns were expressed, however, and the remainder of the audit proceeded normally. Mr. Roy Clarkson, a representative of Georgia Power, reviewed all data to be taken from the site at the exit meeting on 6/24. This information consisted only of the auditor's logbooks and checklists and some blank data forms obtained from Radian. Mr. Al Williams, the Radian Project Manager, made the decision not to release copies of any completed data sheets requested by the auditors based on Georgia Power's concerns.

During one of the meetings with Radian personnel, it was learned that the "major" element(s) for independent mass balance determination had not been selected. This was presumably under negotiation between Radian and DOE as a change in scope.

2. Performance Evaluation Audit

a) Orsat Determination - Mr. Tom Peters of Radian was observed by Mr. Craig Whitaker of RTI while performing the Orsat procedure using test gas supplied by RTI. The audit gas concentration for tank ID number BLM002689 was 9.21% oxygen in dry nitrogen. Correct procedures appeared to be followed. The following data were taken. Acceptable agreement was found for oxygen. Neither carbon dioxide nor carbon monoxide was present in the tank, and none was found.

Replicate	Orsat Result (mL oxygen)
1	9.0
2	9.0
Average:	9.0

Initial volume was 100 mL

9.0 mL/100 mL x 100 = 9.0% found by Orsat.

$$\text{Percent Difference} = \frac{9.0\% - 9.2\%}{9.2\%} \times 100 = -2.17\%$$

b) Performance Audit of Source Sampling Consoles - Mr. Whitaker provided a standardized orifice (ID number 117) to the sampling console operators. They were instructed to set a constant flow using the orifice and to measure the volume indicated by the console's dry gas meter during a 10- or 20-minute sampling period. Operators reported a pressure drop across the RTI orifice, dry gas meter volume, and temperature. Results are tabulated in the following table. "Calculated Volume," the fifth column in the table, was calculated by RTI based on the orifice constant and pressure drop, multiplied by the run time.

CONSOLE (DRY GAS METER VOLUME) PERFORMANCE AUDIT RESULTS*

Radian console serial number	Console location	Run time (min)	Radian console dry gas meter volume (scf)	Calculated volume based on flow using RTI orifice (scf)	Relative Percent difference
A161362	Stack	20	13.98	15.450	- 9.5
A161394	Stack	21	16.59	16.404	1.1
161364	ESP outlet	10	7.89	7.711	2.3
A161395**	ESP outlet	10**	7.50	8.495	- 11.7

* Acceptance criteria ± 10%.

** This audit data set did not include a meter run stop time; however, runs were requested for 10 minutes and the data appear consistent with a 10-minute run time.

c) VOST Sampling - The operator demonstrated extensive knowledge in the operation and process. Cartridges were inscribed with flow directions and encapsulated before and after use. Two sets of tenax and tenax/charcoal were exposed to measured flows of test gas supplied by RTI. Exposure periods were 10 and 20 minutes. Because analytical results must be received before these audit samples can be evaluated, the tube numbers, compounds, and concentrations will be reported in a separate memorandum.

d) Continuous Emissions Monitors (CEMs) - The facility would not allow RTI to audit the installed monitors, but the system functions were explained by the operator, Mr. Jeff Nelms. The cylinders used for daily zero and span checks were found to be Protocol No. 1 gases. Serial numbers and concentrations for these zero/span gases are provided in the following table.

CEM SPAN GAS SUMMARY

Vendor	Cylinder	Compound	Concentration	Expiration date
Scott	AAL-13190	Nitric oxide Sulfur dioxide Nitrogen	360 ppm 1791 ppm balance	5-18-95
Scott	AAL-17497	Oxygen Nitrogen	20.9% balance	5-18-96
Scott	AAL-4472	Sulfur dioxide	241 ppm	1-4-95

Two locations are being monitored by the CEMs: the ESP outlet (immediately upstream of the JBR) and the stack (downstream of the JBR). The following information is being acquired at each location:

ESP outlet (upstream of JBR):
- Temperature
- Opacity
- Oxygen
- NO_x
- SO_2

Stack (downstream of JBR):
- Temperature
- Oxygen
- SO_2

Because different gases are being monitored at the two locations, different span gas combinations and concentrations were used for the span checks. For the stack gas analyzers, cylinder AAL-4472 (SO_2 in N_2) and cylinder AAL-17497 (O_2 in N_2) were used. On the ESP outlet upstream of the JBR, cylinder AAL-13190 (NO and SO_2 in N_2) and cylinder AAL-17497 (O_2 in N_2) were used. Cylinders of zero air were also present for zero determination. According to site personnel, tanks are replaced at intervals of approximately 1 to 2 months. This rather rapid turnover of standard gases is due to the large volume required to fill and purge the hundreds of feet of tubing between the tank, the sampling point, and the analyzers, as described in the next paragraph.

Heated sample lines are used to carry the calibration gas to the probes. The calibration gas then flows back to the CEMs through the same lines that are used acquire gas samples. As part of the audit, the heated sample lines were traced and verified by the operator, who estimated that the fetch (one-way distance from the probe to the CEMs) was 300 to 350 feet. The fetch to the ESP outlet duct probe was estimated to be approximately 600 feet.

3. Technical Systems Audit

The following table summarizes the activities observed by the auditors.

OPERATIONS OBSERVED DURING TSA

Medium	Location	Auditor	Comment
Coal, 1/4" feed	boiler building	Flanagan, Whitaker	Periodic grab samples collected into plastic bucket
Coal, pulverized	boiler building	Flanagan, Whitaker	Cyclone used to capture high-pressure suspension of coal powder prior to burner
Pyrite reject	boiler building	Flanagan, Whitaker	All material caught in plastic buckets
Boiler bottom ash (slurry)	sluice pipe outlet at ash pond	Flanagan, Whitaker	Dipper samples alternately filling two glass carboys

OPERATIONS OBSERVED DURING TSA (continued)

Medium	Location	Auditor	Comment
Condenser water inlet	boiler building	Flanagan	From spigot -- tube allowed to run before sampling
Condenser water outlet	boiler building	not being sampled	Sample point inaccessible
Flue gas	ESP inlet	Whitaker	
Flue gas	ESP outlet	Whitaker	
Stack gas (JBR out)	Stack	Whitaker	
ESP hopper ash (slurry)	sluice pipe outlet at ash pond	Flanagan	Dipper samples alternately filling two glass carboys
JBR makeup water	JBR area	Flanagan	
JBR slurry density	JBR area -- density meter slip stream	Flanagan	Nuclear density meter out of service
Limestone	limestone silo	not observed	
Coal pile runoff	coal pile	not observed	No rain during audit
Cr^{IV} measurement	JBR Project Laboratory	Flanagan	Actual samples not seen; calibration only
XAD-2 cartridge spike for semi-volatiles	laboratory trailer	Flanagan	
Metals train spikes	laboratory trailer	Flanagan	
VOST challenge	stack sampling area	Whitaker	
Orsat procedure (oxygen)	laboratory trailer	Whitaker	Acceptable results.

Recommendations

1. Unusually large differences were seen when RTI's standard orifice was used to test some of the sampling consoles used for source testing. These consoles are scheduled to be re-tested after their return to the laboratory and the results compared with the calibrations prior to the site test. Because of the discrepancies observed with the RTI orifice, the calibration results should be reported to DOE as soon as they are available. The pre- and post-test calibrations must agree within 5% or the data must be corrected. For regulatory purposes, the factor giving the higher emission estimate would be applied; however, for the research work under this project, an average of the two factors would probably be more appropriate.

2. Mass flow rates for solids such as bottom ash and ESP ash are calculated based on coal feed rates and percentage ash in the coal obtained by proximate/ultimate analysis. One or more independent, direct methods of measuring or estimating the amount of ash produced should be attempted. For example, one such method for independently calculating ash production rates would involve multiplying the ash slurry average mass concentration by the length of time the slurry flows and by the flow rate out of the pipe. Ash concentration in the slurry can be obtained by taking representative, time-proportional samples throughout the length of time the slurry flows. Flow rates can be measured at the outfall or obtained from the plant. Intercomparison of different estimates will increase the confidence in the validity of the mass balance calculations. This is a problem common to all contractors at all sites.

3. Because auditors were not allowed to take any completed Radian data sheets off-site, a data audit should be conducted in which raw data sheets, computer-logged data, logbooks, validation procedures, and calculations are examined.

4. A multi-point calibration has not been conducted on the CEMs used for the demonstration project since November 17-20, 1992. The CEMs are not scheduled for another calibration until the next phase of the JBR project, which begins in the fall. This would result in more than a year between calibrations. It is recommended that Georgia Power and Radian make provision to conduct multipoint calibrations at intervals of no more than six months for SO_2, NO_x, and O_2. If possible, line losses between the span gas cylinders and the probes should also be determined at this time.

5. It is recommended that the major elements for mass balance determination be discussed and finalized between DOE and Radian, if this has not already been done.

Personnel Present During Site Visit

Name	*Organization*	*Telephone*
Chuck Schmidt	DOE	(412)892-4690
Tim McIlvried	DOE	
Dave Burford	Georgia Power	(404)253-2111
Roy Clarkson	Georgia Power	
Jeff Nelms	Georgia Power	
Al Williams	Radian	(512)454-4797
Ira Pearl	Radian	(512)454-4797
Barbara Hayes	Radian	(512)454-4797
Renee Cravin	Radian	(512)454-4797
Dave Virbick	Radian	(512)454-4797
Dave Maxwell	Radian	(512)454-4797
Benji Cox	Radian	(512)454-4797
Tom Peters	Radian	(512)454-4797
Ed Zabasaija	Radian	(512)454-4797
Tom Baraga	Radian	(512)454-4797
Jim McGee	Radian	(512)454-4797
Jim Hand	Radian	(512)454-4797
Lori Rodriquez	Radian	(512)454-4797
Jim Flanagan	RTI	(919)541-6417
Craig Whitaker	RTI	(919)541-5988

APPENDIX B: SAMPLING PROTOCOL

Radian used established sampling methods, where possible, to collect representative samples from the various sampling locations within the Yates plant site. The sampling locations at Plant Yates Boiler No. 1 and the various plant processes included:

- Boiler inlet, outlet, and sluice streams;
- ESP inlet, outlet, and ash streams;
- FGD system inlet, outlet, and slurry streams; and
- Stack gas.

For most of the sources, the sampling methods used were standard methods with known performance characteristics, specific for the collection of a representative sample according to the stream matrix. These methods, summarized in Table B-1, provide data for comparisons with industry standards.

Gas Streams

The following section presents the methodology to collect samples from gaseous streams.

Particulate Loading

EPA Reference Method 5[1] or EPA Reference Method 17[2] was performed to determine particulate loading at the selected sampling locations at Plant Yates. Method 5 was used at the stack and ESP outlet locations and Method 17 was used at the ESP inlet sampling location. These methods provided isokinetic extraction of particulate matter on a glass fiber filter. However, since particulate loading determinations were performed in conjunction with the sampling for particulate and vapor-phase metals, quartz fiber filters were used in place of glass. The particulate mass, which included all material that condenses at or above the filtration temperature, was determined gravimetrically, after the removal of uncombined water.

Table B-1
Summary of Sampling Methods

Stream Type	Parameter	Frequency	Sampling Method
Solids	All	Grab sample hourly to composite per test run (time-averaged composite)[a]	EPA Method S007[3] (trowel/scoop)
Liquids	All	Grab sample hourly to composite per test (time-averaged composite)[a]	EPA Method S007 (trowel/scoop) EPA Method S004[4] (tap)
Gases	Volatile Organics	4 pairs of VOST traps over 2-hour time period	VOST (SW-846 Method 0030)[5]
	Semivolatile Organics	Integrated sample over 4- to 6-hour time period	Modified Method 5 (SW-846) Method 0010[6]
	Vapor-Phase Inorganic/ Organic Species	Integrated sample over 4- to 6-hour time period	Various impinger solutions sampling trains
	Trace Elements (Metals)	Integrated sample over 1- to 2-hour time period	Multi-metals sampling train[7]
	Particulate	Integrated sample over 1- to 2-hour time period	EPA Methods 5[8] and 17[9] sampling trains
	Particle Size Distribution	Fixed point sample over appropriate time period	In-stack cascade impactor

[a] Solid and liquid samples for volatile organics analyses were sampled only once per day, per test run.

The RM5 sampling system incorporated a calibrated glass nozzle, heated glass lined probe, heated oven (housing the filter holder and substrate), a condenser assembly, and a calibrated extraction system. The Method 17 sampling system was similar except an in-stack filtration system was used as opposed to the hot box and heated filter holder configuration of Method 5. Both systems operated under vacuum for extraction of effluent gas through leak free components. Both systems were leak checked before and after each individual test.

An extraction (sampling) rate was determined based upon preliminary measurements of temperature, flow rate, pressure, and moisture collected prior to the sampling program. The sampling rate was calculated from these variables to assist in providing and maintaining isokinetic sampling throughout the entire test period. At isokinetic conditions, the velocity of the stack gas entering the nozzle of the extraction system is equal to the effluent velocity at the sample point. The extraction system allowed manual adjustment of the sample rate when changes occurred in any of the variables that would affect isokinetic collection.

The individual stream gas velocities and the selection of the proper sample nozzle dictated the required sample time. The sampling was conducted at equal time intervals along the selected traverse points as determined by EPA Reference Method 1.[10]

After each test sequence, the particulate samples were recovered. For Method 5, the collected sample included the particulate deposited inside the extraction nozzle, heated probe, and filter holder (designated as the front half probe and nozzle rinse, PNR), as well as the particulate collected on the filter substrate. The Method 17 collected sample included the particulate deposited inside the nozzle and collected on the in-stack filter.

Particulate Metals and Vapor-Phase Metals

Sampling for the collection of particulate and vapor-phase metals was performed in conjunction with Method 5 and 17 using the procedures detailed in EPA Conditional Method 29. Method 29 is similar to Method 5 with a few sample train modifications. Modifications to Method 5 included replacing the stainless steel nozzle and probe liner with glass components. Method 17 was modified to operate with a glass nozzle and a teflon coated thimble holder to reduce the possibility of metal contamination due to the sampling system. The particulate material was collected on quartz fiber substrates, replacing the standard glass fiber filters normally used with Methods 5 and 17. Vapor-phase metals were collected in a series of impinger solutions. The first two impingers contained a dilute nitric acid and hydrogen peroxide solution. The third impinger was empty. The next two impingers contained acidic potassium permanganate solution for mercury collection. These impingers were followed by one dry impinger, and an impinger filled with silica gel. A minimum of 100 dry standard cubic feet of gas was collected isokinetically.

Sample recovery was performed in the on-site laboratory. An outline of the sample recovery procedure is detailed below:

1 - Petri dish - plastic - filter

1 - 500 mL glass - Acetone PNR. Rinse front half of filter holder with acetone into PNR bottle.

1 - 500 mL glass - HNO_3 PNR. Rinse front half of filter holder into PNR bottle.

1 - 1000 mL plastic - 1st & 2nd Imp.
Rinse back half of filter holder and impingers with 0.1N HNO_3 into sample bottle.

1 - 1000 mL glass - 3rd, 4th, & 5th impingers. Rinse impingers with 0.1N HNO_3 into sample bottle.

1 - 250 mL glass. Rinse 3rd, 4th & 5th impingers with 8N HCl.

Preservation - None

Particle Size Distribution

The particle size distribution of material in the sample gas was measured using cascade impactors. These impactors classify particulate matter with respect to aerodynamic particle size.

The impactor separated the particulate matter into seven size fractions (six impacted fractions and one fraction collected on the back-up filter). The isokinetic flow rate through the sampling nozzle was determined based on velocity data obtained during earlier sampling (EPA Method 5). Operation of the impactor required the flow rate through the impactor be kept constant. This requirement eliminated the possibility of adjusting the flow rate if variations in stack gas velocity occurred. After sampling, the impactor was unloaded and the collected particulate material weighed. The weight gains were used to calculate the particle size distribution. The recovery outline is presented below:

10 - Petri dishes - plastic - filters
1 - 250 mL glass - acetone PNR. Rinse pre-cutter with acetone into PNR bottle.

Preservation - None

Anions

A Method 5 train was used to collect vapor-phase and solid-phase (particulate) acid gas species of hydrochloric, hydrofluoric, sulfuric and phosphoric acids along with sulfur dioxide and sulfur trioxide. The two sorbing impinger solutions for the acid gases were 200 mL of a carbonate/bicarbonate solution containing hydrogen peroxide followed by a dry impinger and an impinger filled with silica gel. The sample train was operated according to the procedures detailed in EPA Reference Method 5.

Recovery procedures for the Anions train are presented below:

1 - Petri dish - Plastic - filter
1 - 500 mL plastic - H_2O PNR. Rinse front half of filter holder with H_2O into PNR bottle.
1 - 1,000 mL plastic - Impinger contents. Pour the contents of the first three impingers into sample bottle. Rinse back half of filter holder, connecting glassware and impingers with H_2O into sample bottle.

Preservation - Keep cold (< 4°C)

Volatile Organics

The volatile component determinations were performed using a volatile organic sampling train (VOST).[11] In VOST, volatile organics were removed from the sample gas by sorbent traps maintained at 20°C. The first resin trap contained Tenax and the second trap contained Tenax followed by petroleum-based charcoal. A dry gas meter was used to measure the volume of gas passed through the pair of traps. Sample volumes of 20 liters were collected on separate pairs of traps with a 0.5 liter per minute sampling rate. The samples were collected at a fixed point in the stack where the velocity matches the average gas velocity.

The VOST consisted of a quartz probe, water-cooled condensers, sorbent traps, and sample gas metering system. During sample collection, the Tenax traps were maintained at 20°C. To further increase the collection efficiency, the sample gas was cooled and dried by passing it through a water-cooled condenser prior to its contact with the sorbent trap.

Before the initial assembly of the sampling train, all sample-contacting components were cleaned with non-ionic detergent, rinsed in HPLC-grade distilled water, and dried at 100°C. The resin traps were stored in clean glass containers with Teflon-lined screw caps, the condensers and other glassware were covered with appropriate end caps prior to use.

Before use, the traps, the Teflon-filled ceramic ferules, and the hardware used in connecting the traps, were conditioned. The virgin Tenax and the charcoal were Soxhlet extracted with methanol. After the resins were dried under infrared lamps, they were placed in a vacuum oven for six hours at 50°C. The tubes were packed individually and thermally conditioned for 12 hours at 200°C with organic free nitrogen at a rate of 40 mL/min. To check for emissions of volatile organic compounds, a tube from each batch was tested as a blank.

Leak checks were performed before and after collection of each pair of resin traps. After the post-collection leak check had been completed, the traps were sealed with end caps and returned to their respective glass containers for storage and transport. During storage and transportation, the traps were kept cool (< 4°C).

Aldehydes

Aldehydes were collected using a 2,4-dinitrophenylhydrazine (DNPH) train according to EPA Method 0011.[12] Sample collection was performed isokinetically following the procedures detailed in EPA Method 5. The impinger solutions were combined into one sample along with the methylene chloride glassware rinse. The solutions were sealed in amber glass containers with Teflon closures and stored at 4°C.

Semivolatile Compounds

Semivolatile organics (SVs) determinations were performed using a Modified Method 5 (MM5)[13] sampling train. The probe washes, filter catches, XAD sorbent traps, and aqueous condensates were extracted and analyzed for SVs according to SW-846 Method 8270 protocol. The MM5 sampling system consisted of a heated probe, heated filter, sorbent module, and pumping and metering unit. A gooseneck nozzle of an appropriate diameter to allow isokinetic sample collection was attached to the probe. S-type Pitot tube differential pressure was monitored to determine the isokinetic sampling rate.

From the heated filter, sample gas entered the sorbent module. The sorbent module consisted of a water-cooled condenser followed by the XAD-2 resin trap. After the resin trap was a dry, modified Greenburg-Smith impinger which collected the aqueous condensate. The stem of this impinger was short to reduce carryover of collected aqueous condensate. Following the condensate trap were two water impingers that collected any mist carryover from the condensate trap, and a final impinger containing silica gel to dry the sample gas before metering. A pump and dry gas meter were used to control and monitor the sample gas flow rate.

Sampling of the stack gases was conducted in accordance with the published MM5 protocol. The sampling rate for each train was between 0.5 and 1.0 dscfm. A minimum of 106 dscf was collected by each train over a minimum sampling period of two hours.

Sampling train preparation and sample retrieval were performed in a controlled environment to reduce the possibility of sample contamination. Prior to assembly, each component of the sampling train was thoroughly rinsed with methylene chloride.

After sample collection, the ends of the sampling train were sealed with solvent-rinsed foil and returned to the clean-up area for sample retrieval. The filter was recovered and placed in a methylene chloride-rinsed glass petri dish. Aqueous condensate collected in the first two impingers and in the sorbent trap was transferred to methylene chloride-rinsed amber glass bottles with Teflon-lined screw cap closures. All components of the sampling train, from the nozzle through the sorbent module, including the probe, filter glassware, and impinger glassware were rinsed thoroughly with a solution of methylene chloride. The probe was cleaned using a nylon brush followed by rinsing with a methylene chloride. The probe rinse and glassware rinses were combined with the recovered condensate sample. The XAD-2 resin cartridges were sealed and transferred to the laboratory intact. The recovery procedures are outlined below:

1 - Petri dish - glass - filter
1 - 500 mL glass - $MeCl_2$ PNR. Rinse front half of filter holder with $MeCl_2$ into PNR bottle.

1 - XAD Resin Cartridge
1 - 500 mL glass - Condensate. Pour the contents of the first two impingers into bottle. Discard third impinger H_2O_2 solution.
1 - 500 mL glass - $MeCl_2$ Train Rinse. Rinse back half of filter holder, condenser, connecting glassware and impingers 1 and 2 with $MeCl_2$ into sample bottle.

Preservation - Keep cold (< 4°C)

Dioxins and Furans

Sampling for the collection of dioxins and furans present in the selected gas stream was performed using EPA Reference Method 23.[14] Sample collection procedures specified in Method 23 were followed with the following exception:

- All train component rinses were performed with methylene chloride and acetone. An additional toluene rinse was then performed and added to the respective front half and back half acetone/methylene chloride rinse samples.

Sample rate, volume and procedures were identical to the MM5 procedures described above.

Ammonia

Sample collection for the determination of ammonia present in the gas streams was performed in conjunction with the anions sampling train. Similarly as with the anions sample train, gas was extracted isokinetically through a glass fiber filter then directed to an impinger train which contains the collection solution. For the collection of ammonia, dilute sulfuric acid was placed in the first two impingers of the condenser assembly. Recovery procedures for the ammonia train are presented below:

1 - 1,000 mL plastic - Impinger contents. Pour the contents of the first three impingers into sample bottle. Rinse connecting glassware and impingers with H_2O into sample bottle.

Hydrogen Cyanide

Sample collection for the determination of hydrogen cyanide present in the gas streams was performed in conjunction with the ammonia sampling train. Gas was extracted isokinetically through a glass fiber filter then directed to an impinger train which contains the collection solution. For the collection of cyanide, dilute zinc acetate solution was placed in the third and fourth impingers of the ammonia train. Recovery procedures for the hydrogen cyanide portion of the train are presented below:

1 - 1,000 mL glass - Impinger contents. Pour the contents of the first three impingers into sample bottle. Rinse connecting glassware and impingers with H_2O into sample bottle.

Radionuclides

Flue gas particulate samples for radionuclide analysis were collected using the approach defined by EPA Reference Methods 5 and 17 with one exception. The samples were collected at a single point in the duct representative of the average flue gas velocity. Filter samples were stored and transported in plastic petri dishes and thimbles were contained in plastic bottles.

Extractable Metals

Separate samples for extractable metals content were also collected using the single point isokinetic approach described for radionuclide sample collection. Quartz-fiber filter media was used to reduce the background metals contribution associated with glass fiber filters. Filter samples were stored and transported in glass petri dishes and thimbles were contained in glass bottles.

Vapor-Phase Mercury by Charcoal Sorption

Sampling for mercury speciation was performed using a sample train designed by Nicolas Bloom.[15] The sampling train consists of a quartz probe, tandem pair of soda-lime traps, tandem iodated carbon traps, drierite cartridge and mass flow metering system. The sample train was assembled outside of the stack and leak checked to verify the sample integrity. The probe tip was placed at a single point in the stack that was determined to be representative of normal flow, based upon preliminary velocity measurements. The sample was extracted from the source with the sample rate adjusted to provide a 100 Liter sample collected over a minimum of two hours. At the completion of sampling, the train was leak checked and the sorbent tubes and probe liner recovered. Sorbent tubes were segregated based upon run and location and sealed in plastic bags for transport to the laboratory.

Chrome VI

Samples were collected via the BIF method for chromium (VI).[16] This method used a nozzle, teflon lines, peristaltic pump for recirculating solution and impinger solutions. The impinger contained a known volume of 10 N potassium hydroxide. Samples were collected isokinetically from the outlet stack using the sampling procedures detailed in EPA Reference Method 5. At the completion of the sample collection period, the sample train was purged with ultrapure nitrogen prior to the recovery of the sample. The impinger solutions were recovered from the sample train, filtered, then transported to the on-site laboratory for analysis. All of the train components were rinsed with 0.1N nitric acid and the rinse was retained for total chromium analysis.

Solid Sampling Procedures

Dry solid stream samples (raw coal, boiler feed coal, pulverizer rejects, limestone, and ESP hopper ash) were collected using grab sampling techniques. Individual grab samples of each stream were collected hourly throughout each test run and composited to generate a representative, time-averaged composite sample. Composite samples of raw coal, boiler feed coal, pulverizer rejects, and raw limestone were riffled and split to produce a 1 kilogram (minimum) sample which was placed in a plastic bag and sealed for transportation to the laboratory.

Two composite samples of dry fly ash, one for each ESP field, were prepared from individual grab samples collected from ESP hoppers 1-4, and 5-8. For purposes of compositing, the mass distribution and removal efficiency were assumed to be uniform across the ESP inlet duct and across each bank of ESP ash hoppers. Consequently, the ash collected from each of the four hoppers in the same field were composited equally. Each composite sample was thoroughly mixed and stored in pre-cleaned glass bottles (for analysis of organic compounds), or in plastic bottles. Samples collected for organic compound analyses were refrigerated at 4°C and kept cool during transportation to the laboratory. No preservation was needed on samples for inorganic analyses.

Sluiced ash stream samples (bottom ash and ESP fly ash) were also collected using grab sampling techniques. Bottom ash, which is normally sluiced once per shift at Plant Yates, was sluiced prior to the beginning of each daily test run to remove accumulated ash material that was non-representative of the test period. Bottom ash sluicing operation was then secured immediately before, and throughout each daily test period. At the conclusion of each test period, sluicing operations were resumed while a sampler collected multiple grab samples with a polyethylene dipper. Samples were collected as long as there was visual evidence of bottom ash in the sluice water at concentrations high enough to warrant continued sampling.

These samples were composited directly into a large bucket where the ash was allowed to settle. After the ash had settled, the sluice water component was siphoned off to avoid disturbing the ash fines, and the wet ash mixed and bottled for storage and transportation to the laboratory. Samples for analysis of organic compounds were split from the composite sample and preserved in pre-cleaned, amber-glass containers by cooling to 4°C.

Sluiced fly ash from the ESP hoppers was collected in a manner similar to bottom ash, except sluicing operations were performed continuously to avoid ash buildup in the ESP. Since the ESP ash sluicing system was combined with the sluiced economizer and air preheater ash, the systems were isolated before the start of the test run to avoid bias in the ESP ash composite. Grab samples were collected hourly from the sluice water discharge pipe to the ash pond. Like bottom ash, the fly ash was allowed to settle, and the sluice water component siphoned off to avoid disturbing the ash fines. The wet ash was mixed and bottled for storage and transportation to the laboratory. Samples for analysis of organic compounds were split from the composite sample and preserved in pre-cleaned, amber-glass containers by cooling to 4°C.

Limestone and FGD slurry samples were collected using grab-tap sampling procedures. Sample taps were opened and allowed to purge immediately prior to collecting the process samples to insure representative sample collection. Hourly grab samples of limestone slurry were composited directly to a large container, and FGD slurry was filtered directly from the tap through a filter press. The limestone slurry composites were filtered after mixing. The recovered filter cakes were bottled for storage and transportation to the laboratory. Samples for analysis of organic compounds were split from the composite samples and preserved in pre-cleaned, amber-glass containers by cooling to 4°C. Sub-samples of the FGD solids composite were also taken for the on-site analysis of sulfite and sulfate ions.

Liquid Sampling Procedures

Liquid samples were collected from both filtered and unfiltered sources. Raw, unfiltered water streams consisted of ash pond water, recycled gypsum pond water, coal pile run-off, and cooling water at the inlet of the steam condenser. Filtered streams consisted of bottom ash and fly ash sluice water, and limestone and FGD slurry filtrates.

Raw water samples were sampled by grab-tap sampling techniques. Hourly grab samples were composited into appropriate sample containers and preserved as soon as possible after sample collection. In some cases the sample was added directly to sample bottles containing the preservative in order to reduce the loss of the more volatile species (e.g. NH_3, CN^-). Table B-2 presents the liquid sample preservation techniques for specific analytes.

Filtrate samples were collected as described in the corresponding sluice water or slurry stream. Sluice water that was siphoned from the settled ash material was filtered in its entirety, split into the appropriate sample containers, and preserved according to the techniques presented in Table B-2. Slurry filtrates were also split into appropriate containers and preserved in the same manner as sluice water filtrates.

Sluice water and slurry filtrate samples collected for the analysis of volatile organic compounds and aldehydes present the only exception to the sample collection procedures described above. Due to the volatility of these analytes, bottom ash sluice water, ESP fly ash sluice water, limestone slurry, and FGD slurry samples were collected for volatile organics directly into VOA vials without filtration, and chilled to 4°C.

References

1. 40 CFR 60, Appendix A. *Test Methods.* "Method 5: Determination of Particulate Emissions from Stationary Sources."
2. 40 CFR 60, Appendix A. *Test Methods.* "Method 17: Determination of Particulate Emissions from Stationary Sources (In-Stack Filtration Method)."
3. U.S. Environmental Protection Agency. "Method S007: Solid Grab Sample, Trowel (Scoop)," *Sampling and Analysis Methods for Hazardous Waste Combustion.* EPA-600/8-84-002 (February 1984).
4. U.S. Environmental Protection Agency. "Method S004: Liquid Grab Sample, Tap," *Sampling and Analysis Method for Hazardous Waste Combustion.* EPA-600/8-84-002 (February 1984).

5. U.S. Environmental Protection Agency. Office of Solid Waste. "Method 0030: Volatile Organic Sampling Train," *Test Methods for Evaluating Solid Waste.* SW-846, 3rd ed., Washington, D.C. (November 1986).

6. U.S. Environmental Protection Agency, Office of Solid Waste. "Method 0010: Modified Method 5 Sampling Train," *Test Methods for Evaluating Solid Waste.* SW-846, 3rd. ed. Washington, D.C. (November 1986).

7. 40 CFR 266, Subpart H, "Method 29: Determination of Metals Emissions in Exhaust Gases from Hazardous Waste Incineration and Similar Combustion Processes: Proposed Method."

8. 40 CFR 60, Appendix A. *Test Methods.* "Method 5: Determination of Particulate Emissions from Stationary Sources."

9. 40 CFR 60, Appendix A. *Test Methods.* "Method 17: Determination of Particulate Emissions from Stationary Sources (In-Stack Filtration Method)."

10. 40 CFR 60, Appendix A. *Test Methods.* "Method 1: Sample and Velocity Traverses from Stationary Sources."

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12. 40 CFR 266, Appendix IX, Section 3.5. *Methods Manual for Compliance with the BIF Regulations.* "Sampling for Aldehyde and Ketone Emissions from Stationary Sources (Method 0011)."

13. U.S. Environmental Protection Agency. Office of Solid Waste. "Method 0010: Modified Method 5 Sampling Train," *Test Methods for Evaluating Solid Waste.* SW-846, 3rd ed., Washington, D.C. (November 1986).

14. 40 CFR 266, Appendix IX: *Methods Manual for Compliance with the BIF Regulations.* "Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Stationary Sources (Method 23)."

15. Bloom, Nicolas S., Eric M. Prestbo, and Vesna L. Miklavicic. "Fluegas Mercury Emissions and Speciations from Fossil Fuel Combustion." Published in the proceedings of the Second International Conference on Managing Hazardous Air Pollutants. Sponsored by the Electric Power Research Institute. Washington, D.C. (July 1993).

16. 40 CFR 266, Appendix IX: *Methods Manual for Compliance with the BIF Regulations.* "Determination of Hexavalent Chromium Emissions from Stationary Sources (Method Cr^{6+})."

Table B-2
Preservation, Storage, and Holding Time Requirements for Liquid Samples

Analytical Parameter	Preservation and Storage Requirements	Maximum Holding Time (Days)
Volatile Organics	Cool 4°C; amber glass VOA vial	7 analyze
Semivolatile Organics	Cool 4°C; amber glass	14 extract, 40 analyze
Formaldehyde	Cool 4°C; amber glass	5 derivitize, 3 analyze
Soluble Metals	Filter on-site; HNO_3 pH < 2	6 months analyze[a]
Total Metals	HNO_3 pH <2; plastic	6 months analyze[a]
Anions	Cool 4°C; plastic	28 analyze
Phosphate	Cool 4°C; H_2SO_4 to pH <2	28 analyze
Sulfite	None; plastic	Analyze immediately
Ammonia	Cool 4°C; H_2SO_4 to pH <2	28 analyze
Cyanide	Cool 4°C; NaOH to pH >12	14 analyze

[a] Maximum holding time for Hg is 28 days.