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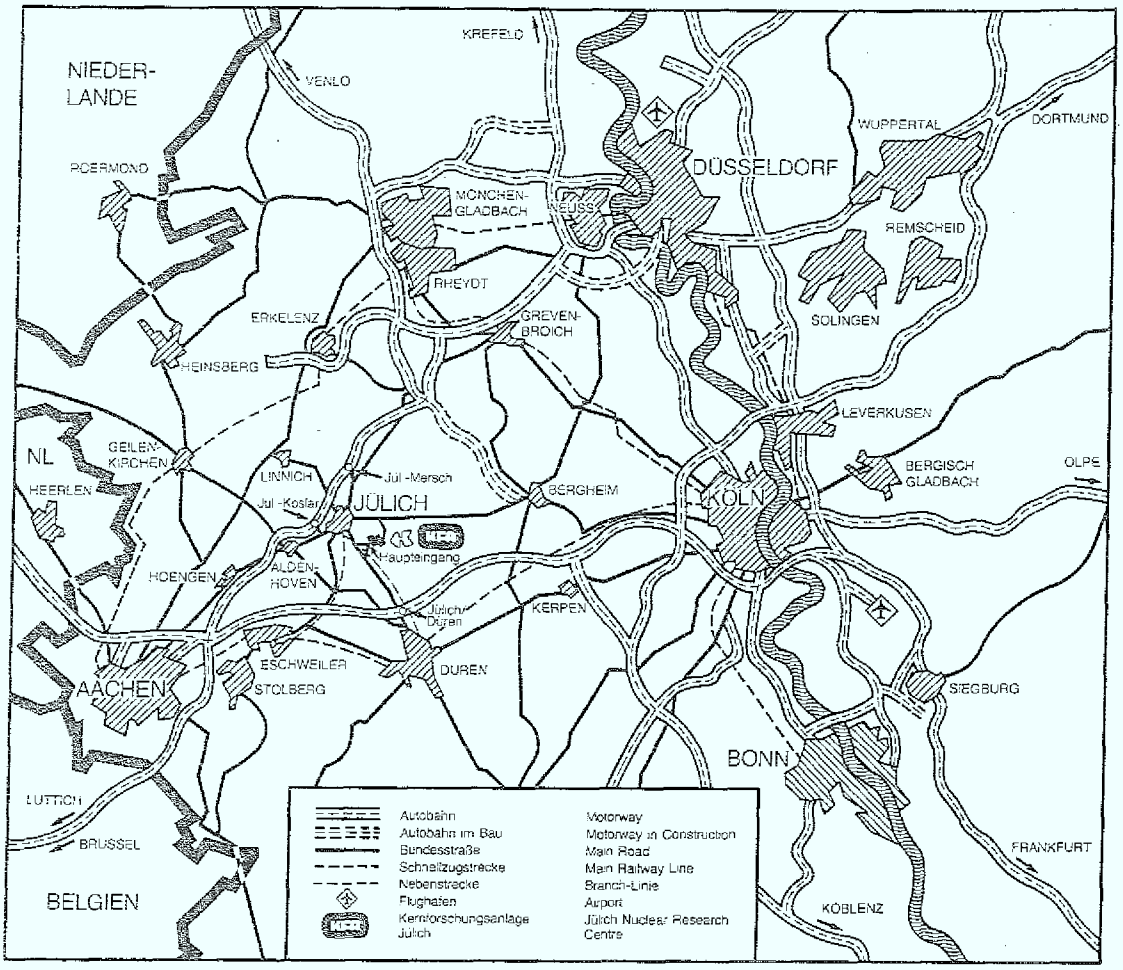
EVALUATION OF MASS BALANCE INVESTIGATIONS IN COAL-FIRED POWER PLANTS

by

Tina Masterson
Heidrun Barnert-Wiemer

Jül-2160
October 1987
ISSN 0366-0885



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Institut für Chemische Technologie der Nuklearen Entsorgung Jül-2160

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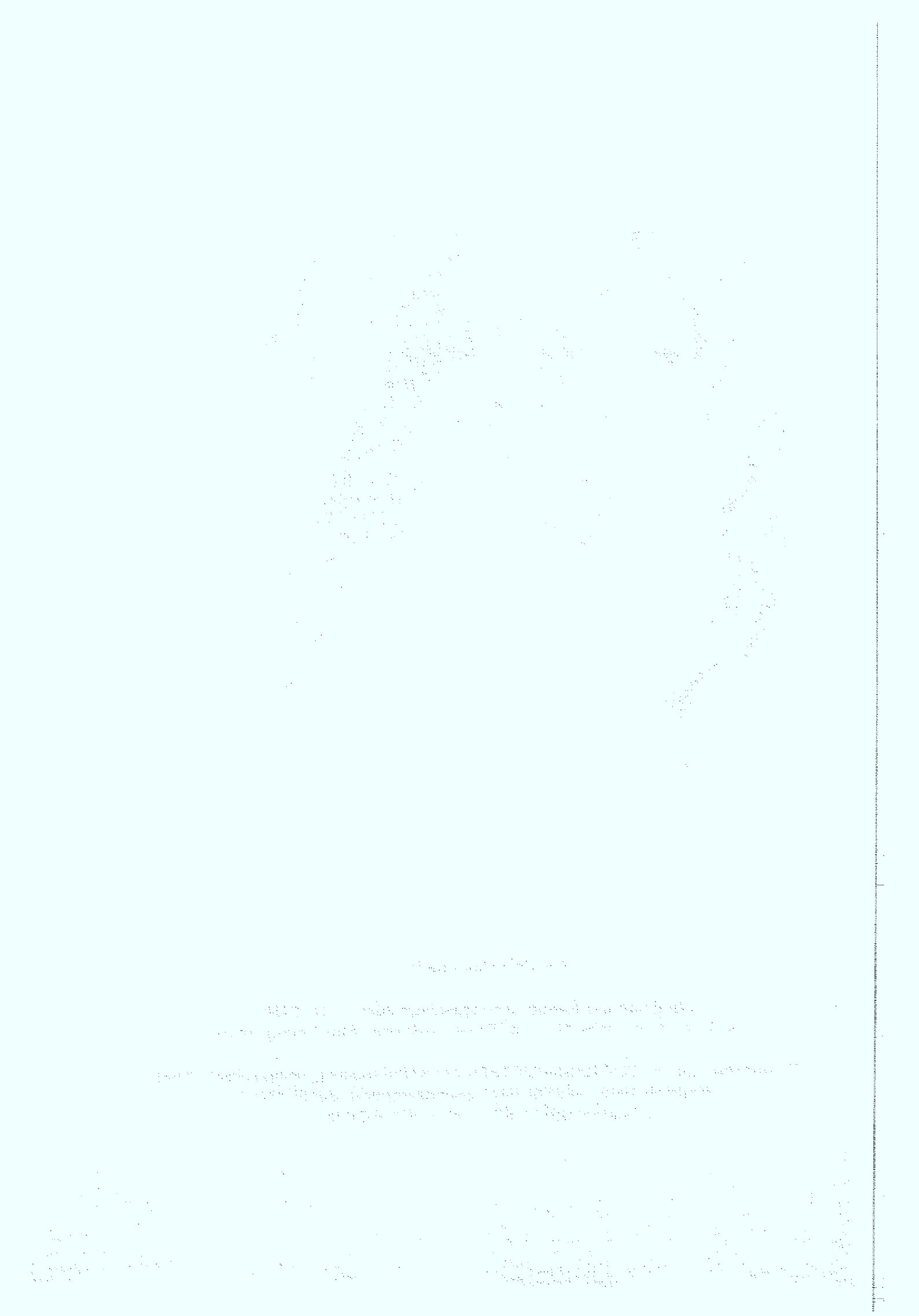

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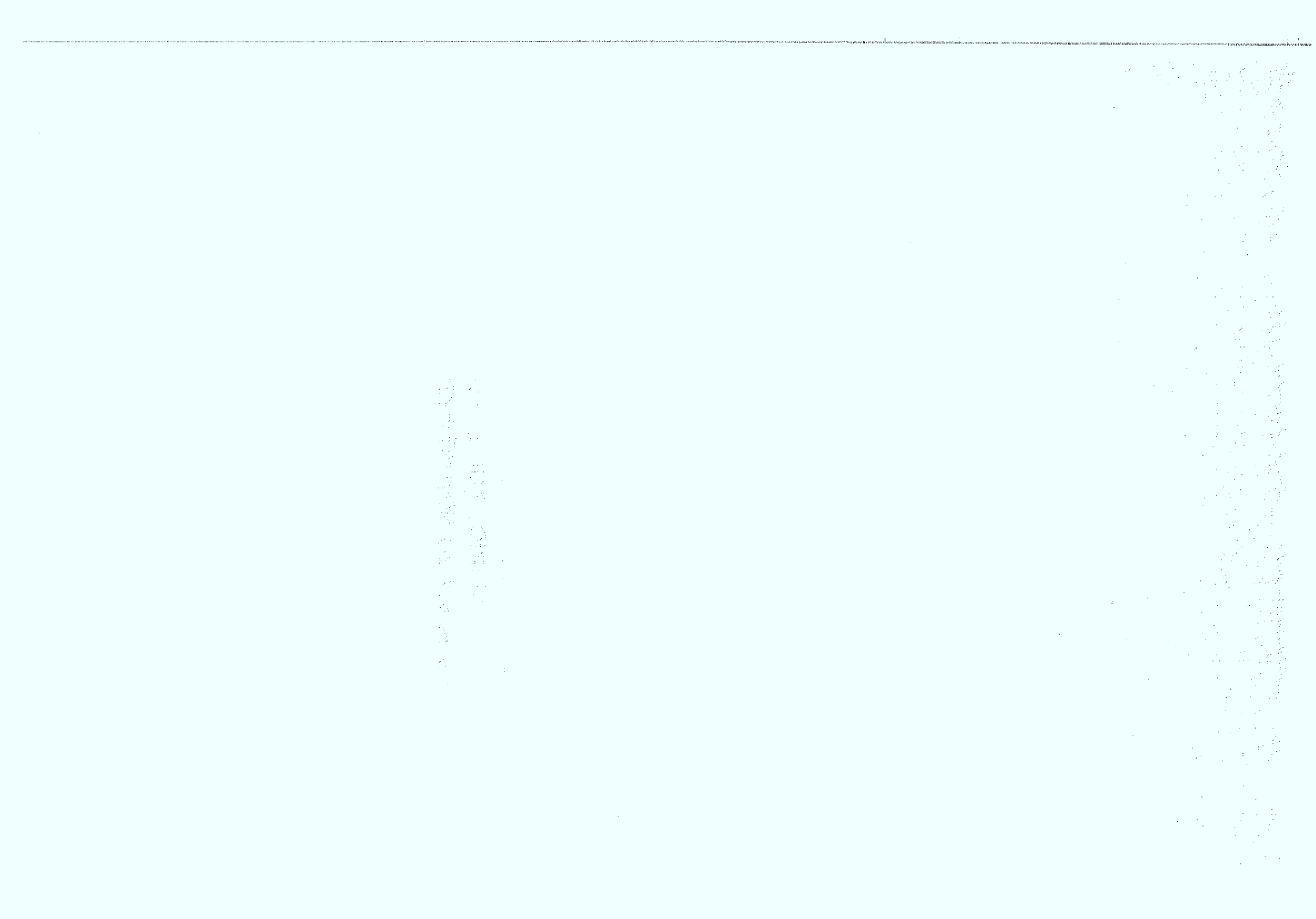

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ABSTRACT

Coal contains trace quantities of many elements that can be toxic if present in high enough concentrations. Many of these elements are released after combustion into more available forms for human assimilation. Hence, burning coal increases the potential for toxic trace element hazard. Assessment of the literature on measurements of trace elements during the combustion of coal has made it clear that these measurements are imprecise and contradictory.

In this literature review, mass balance measurements in coal-fired plants are evaluated and research in the enrichment of trace elements in coal ashes is reviewed. The problems in measuring trace elements in coal-fired facilities are presented with the intention that the knowledge of the difficulties outlined here will promote future study and active research in these areas.

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1. Introduction

Coal contains trace quantities of many elements that can be toxic if present in high enough concentrations. Many of these elements are released after combustion into more available forms for human assimilation. Hence, burning coal increases the potential for toxic trace element hazard. The question is, does this release directly or indirectly affect human welfare? This can not be answered on the basis of present data. Assessment of the literature on measurements of trace elements during the combustion of coal has made it clear that they are imprecise and contradictory. There is little if any data to compare emissions of industrial boilers, and present data is too inconsistent to permit even generalized conclusions. Eventually there must be a unification and improvement on more basic levels in methods of sampling , analytical techniques, and data handling before greater assessment of emissions of coal-fired facilities can be examined.

In this literature review, mass balance measurements in coal-fired plants are evaluated and research in the enrichment of trace elements in coal ashes is reviewed. The problems in measuring trace elements in coal-fired facilities are presented with the intention that the knowledge of the difficulties outlined here will promote future study and active research in these areas.

2. Trace Element Mass Balance Comparisons Between Coal-Fired Plants

It is difficult to evaluate and compare systematically mass balances in full-scale boiler because of the variations in coal composition and operating conditions. Most trace element determinations have been done on combustion fractions in pulverized-coal combustion (PCC) boilers 250 MW(e) or larger that are used for power generation. Trace element studies during fluidize-bed combustion are fewer compared to PCC (Littlejohn, 1984).

Essentially, there is not enough available information in the literature to present a comparison of trace element behavior during combustion in similar boiler types. The types of coal-fired power plants that have been studied vary in net capacities (250, 622, 750, 870 MW(e)), types of emission controls, and the coal fired. Therefore, any comparison would have to be

greatly generalized. An additional problem in trace element analyses of coal-fired facilities is variations within the same plant. Flow rates can vary within the same facility. Fly ash removal by a precipitator may be better at different operating times. Even trace elements in coals can vary between mines and in the same coal bed, thus making composition of combustion products different (Kaakinen et al., 1975; Klein et al., 1975; Norton et al., 1986). But before any major comparison of coal-fired facilities is appropriate, there has to be the solving of fundamental problems in the measurement of trace elements in coal-fired plants. Improvement in methods of sampling, analytical technique and data handling will render a more accurate determination of trace element mass balances and subsequent comparison of coal-fired facilities.

3. Literature Review of Previous Mass Balance Studies in Coal-Fired Plants

To begin a discussion of previous mass balance investigations, it is appropriate to review a state of the art comprehensive study done by Klein et al. (1975) and then examine the more recent principal mass balance investigations that have been performed to assess the flow of trace elements through coal-fired power plants (Kaakinen and Jorden 1974; Heinrichs, 1977, 1982; Meserole et al., 1979; Zielke and Bittman, 1982; Klusek et al., 1983; Tadmor, 1986), with emphasis on the location of sampling and the type of data reported and utilized in the mass balance determinations. Finally, this review will discuss the problems with mass balance determinations and evidence for improvements in measurements.

The study by Klein et al. (1975) was done to determine emission characteristics and obtain mass balances for thirty-seven trace elements for the Tennessee Valley Authority 870 MW(e) Thomas A. Allen Steam Plant in Memphis, Tennessee. The mass balance measurements for the Allen Steam Plant were done using samples of coal, precipitator inlet and outlet fly ash, and slag tank solids. The data required for mass balance calculations were concentrations of elements in each stream and the total flow rate of each stream (g/min). Imbalances are calculated using the following formula:

% Imbalance = (slag flow + fly ash flow + gas flow - coal flow)/ coal flow multiplied by 100

Sampling was also performed on the precipitator outlet flue gas to evaluate precipitator efficiency for various elements, thereby providing some measure of atmospheric discharges. The authors considered the flow of trace elements into the plant with any suspended particulate in inlet air or slurry water as negligible in the mass balances. The balances for some elements are respectable (Table 1). For others the results showed much greater negative and positive imbalances for the two sets of runs performed during January, 1972 and August, 1973. Serious negative imbalances occurred for the elements Br and Cl. It was noted that the impinger solutions for gas collection were not analyzed for these elements. Positive imbalances occurred for Cr and V, suggesting that an excess in the fly ash was due to corrosion of the boiler tubes. The imbalances of the volatile elements were thought to be due to the flue gas sampling method that was designed primarily to collect particulates efficiently. Arsenic was reported in the 1972 sampling to have a large negative imbalance, whereas, those values obtained in 1973 gave an equally large positive imbalance. It was tentatively concluded that since very little arsenic was found in the impinger solutions, then arsenic was minimal in the vapor phase and imbalances were due to sampling or analytical difficulties. However, the large negative imbalance (-57%) could imply the reverse: that a substantial portion of this element was in the vapor phase of the flue gas and not adequately sampled.

The character of trace element partitioning within a single pulverized coal-fired power plant, the 180 MW(net) Unit No. 5 of the Public Service Company of Colorado's Valmont Power Station near Boulder, Colorado, was investigated by Kaakinen and Jorden (1974). Sampling was performed on all potientially significant inlet and outlet streams of trace elements at about the same time. These included coal; bottom ash; ash from the mechanical collector hopper and electrostatic precipitator hopper; fly ash from flue gas at the scrubber inlet, scrubber outlet, and electrostatic precipitator outlet; scrubber slurry; and scrubber makeup water. No gaseous trace elements in the flue gas were successfully sampled. Total mass flow rates (the solid and/or liquid flow at each point, averaged for three runs) were calculated, and mass balances were done using only 11 elements for which a full set of mean concentrations had been obtained (Table 2). Generalized results were reported for element concentrations that were essentially constant in all outlet ashes, depleted in bottom ash, or increased in fly ash collected downstream. Large imbalances were found for Se and Hg supporting the theory that major portions of inputs of these elements left as vapors or very

Table 1: Trace element flows through a coal-fired power plant. (After Klein et al., 1975)

Element		Element flow, g/min				Imbalance %	Atmospheric discharge g/min
		Coal	Slag	Inlet fly ash	Inlet gas		
Al	72	14,000	10,400	3,600		0	400
Al	73	15,340	8,620	6.720		0	30
As	72	5.3	0.5	1.8		− 57	0.2
As	73	6.5	1.5	8.1	< 0.1	+ 48	0.2
Ba	73	96	42	55		+ 1	0.3
Br	73	5.4	0.2	0.3		− 90	~ 6
Ca	72	5,200	4,000	1,000		− 4	20
Ca	73	6,380	3,880	2,360		− 2	10
Cd	72	0.58	0.42	0.30		+ 24	0.01
Cd	73	0.69	0.09	0.59	< 0.05	− 1	0.02
Ce	73	12.1	7.1	6.2		+ 10	0.04
Cl	73	1340	8	15		− 98	~ 1,300
Co	72	4.9	2.7	2.1		− 2	0.04
Co	73	4.3	1.8	2.9		+ 9	0.02
Cr	72	27.5	21.2	14.0		+ 28	
Cr	73	26	13	22		+ 33	0.3
Cs	72	1.9	1.1	0.9		+ 5	
Cs	73	1.6	0.6	1.0		0	0.01
Cu	73	12.2	1.7	10.3		− 2	
Eu	72	0.30	0.15	0.10		− 17	
Eu	73	0.15	0.09	0.09		+ 20	0.0005
Fe	72	19,700	14,800	6,100		+ 6	200
Fe	73	15,950	9,440	8,940		+ 16	60
Ga	73	6.6	0.4	6.0		− 3	
Hf	73	0.59	0.39	0.30		+ 17	0.002
Hg	73	0.18	0.002	0.004	0.17	0	0.1 (gas only)
K	72	2,700	1,550	850		− 11	20
K	73	2,260	1,330	1,480		+ 24	9
La	72	6.5	5.5	1.8		+ 12	0.04
La	73	5.6	3.5	3.0		+ 16	0.02
Mg	72	2,000	1,400	620		+ 1	50
Mg	73	1,780	1,040	780		+ 2	
Mn	72	66	56	18		+ 12	0.8
Mn	73	49.7	24.9	22.0		− 6	0.2
Na	72	840	420	320		− 12	8
Na	73	1,020	420	750		+ 15	4
Ni	73	23	7	16		0	
Pb	72	9.2	0.6	7.8		− 9	0.2
Pb	73	7.2	0.5	5.9	< 0.1	− 11	0.2
Rb	73	22.8	8.6	11.5		− 12	0.07
Sb	73	0.74	0.05	0.89	< 0.1	+ 27	0.2
Sc	72	4.2	2.8	1.5		+ 2	0.2
Sc	73	3.2	1.8	1.9		+ 16	0.01
Se	73	3.2	0.0	1.8	0.53	− 22	0.4
Si	73	33,960	19,300	14,480		− 1	
Sm	73	1.47	0.69	0.78		0	0.003
Sr	73	34	14	18		− 6	
Ta	73	0.16	0.08	0.10		+ 12	0.0007
Th	73	3.1	1.3	1.5		− 10	0.01
Ti	72	680	390	230		− 9	6
Ti	73	740	340	440		+ 5	4
U	72	3.0	2.0	1.1		+ 3	0.02
U	73	3.20	1.26	2.22		+ 8	
V	72	45	34	23		+ 24	0.8
V	73	41.9	21.9	32.5		+ 30	0.4
Zn	72	120	3	78		− 35	2
Zn	73	68	8.4	55	< 1.0	− 7	2

Table 2: Closure of mass balances. (After Kaakinen and Jorden, 1974)

Element	Analytical Method	Relative Imbalance (%)	
		Based on analyses of ashed coal	Based on analyses of whole coal
Mo	Color.	+ 10	
Mo	XF	− 4	
Fe	AA	− 7	
Fe	XF	− 13	− 18
Rb	XF	− 25	− 35[a]
Sr	XF	− 17	− 17
Y	XF	− 7	− 15
Zr	XF	− 20	− 38
Nb	XF	− 16	− 13[a]
^{210}Pb	Rad.	+ 23	
^{210}Po	Rad.	+ 21	
Cu	XF	+ 11	+ 70[a]
Zn	XF	+ 9	+ 55[a]
As	XF	− 1[a]	+ 46[a]
Se	XF	− 220[a]	+ 62
Sn	XF	+ 45[a]	+ 88[a]
Pb	XF	+ 13[a]	
^{226}Ra	Rad.	− 60[a]	

[a]Values involving analyses for which inaccuracies or imprecisions are indicated to be a problem.

Color. – Colorimetric
AA – Atomic Absorption Spectrophotometry
XF – X-ray Fluorescence
Rad. – Radiochemical analysis

fine particles in the flue gas.

Tadmor (1986) has recently performed an involved material balance computation on radioelements 210Pb, Th and U, using data from Klein et al. (1975), Kaakinen et al. (1975), and Horton et al. (1977). The material balances were computed using activity or concentrations previously measured in the input coal and in the different fractions of ash produced in the coal-fired plants. These activities combined with the percentages of different

plant. Samples were obtained from the brown coal, inlet and outlet precipitator ash and bottom ash from three boilers. Calculation of coal feed rate and the flow rates of slag and precipitator ash were done from the plant metering system and corrected to dry weight. Percent imbalances were calculated using the formula:

$$\% \text{ Imbalance} = \frac{\text{Precipitator Inlet Ash} + \text{Bottom Ash} - \text{Brown Coal}}{\text{Brown Coal}} \times 100$$

Percent imbalances (Table 4) were in general negative for most elements and for Cr, Fe, Sc, V and Zr positive. It was concluded that the excess of these elements in the fly ash was possibly due to corrosion of the pipes. Negative imbalances for As, Bi, Cd, Cl, F, Hg, P, Pb, S, Se, Tl and Zn were thought to have originated from less efficient retainment by electrostatic precipitation. The elements were found to be "remarkedly enriched" in the outlet fly ash. The elements Cl, F, Hg and S were thought to have been primarily discharged to the atmosphere as gases. A rough estimate is given for values of the annual nation-wide trace element emissions due to brown coal combustion for power production (Table 5). The emission values are only for the elements in the flue gas that were less well removed by electrostatic precipitators. It was noted that there is a lack of information in what form the metals are emitted and that chlorine and fluorine possibly participate in the transport of these metals. Chlorides are known to have a high vapor pressure and to take part in the transport of heavy metals (Ahlheim and Romer, 1984). In addition, chlorides are found to be the most volatile naturally occurring compounds for most metals (Krauskopf, 1979). As of yet, the extent of the role of chlorine and fluorine in the transport of metals in the fly ash and flue gas has not been determined.

A study to characterize the routes of twenty-seven trace elements through four coal-fired power plants equipped with various ash control devices was performed by Meserole et al. (1979). Elemental material balances were used to verify the measured trace element flows in each of the outlet streams. All inlet and outlet process streams were sampled. The exit streams included bottom ash, collected fly ash, and vapors in the exhausted flue gases. The flow rate and analytical trace element concentration data were used to calculate the amount of trace element that was entering or exiting the plant in various streams. Closure of these

Table 4: Trace element flows through a brown coal fired power plant.
(After Heinrichs, 1982)

	Element flow, kg/day				
	Brown coal	Precipitator inlet ash	Bottom ash	Imbalance %	P.O.A. / P.I.A.
Al	1.46×10^5	1.38×10^5	6.75×10^3	− 1 (± 1)	1.8
As	4.36×10^1	3.71×10^1	8.25×10^{-1}	−13 (± 3)	5.2
Ba	1.71×10^3	1.62×10^3	3.83×10^1	− 3 (± 2)	1.8
Be	1.84×10^1	1.72×10^1	2.74×10^{-1}	− 5 (± 2)	1.7
Bi	5.61×10^{-1}	4.05×10^{-1}	6.74×10^{-3}	−27 (± 8)	5.9
Ca	4.99×10^5	4.42×10^5	5.21×10^4	− 1 (± 1)	1.7
Cd	1.12	8.44×10^{-1}	1.46×10^{-2}	−23 (± 6)	4.4
Ce	1.71×10^2	1.52×10^2	1.65×10^1	− 1 (± 1)	1.9
Cl	2.06×10^4	1.05×10^3	1.09×10^2	−94 (± 4)	9.1
Co	6.86×10^1	6.75×10^1	2.70	+ 2 (± 1)	1.4
Cr	1.99×10^2	1.99×10^2	7.88	+ 4 (± 2)	1.9
Cu	6.54×10^1	6.41×10^1	1.05	0 (± 1)	2.7
Dy	1.18×10^1	1.15×10^1	3.41×10^{-1}	0 (± 1)	1.3
F	2.93×10^3	7.43×10^2	2.55×10^1	−74 (±11)	6.6
Fe	1.68×10^5	1.76×10^5	1.58×10^4	+14 (± 6)	2.0
Gd	4.36×10^1	4.05×10^1	9.00×10^{-1}	− 5 (± 1)	1.8
Hg	3.43	4.05×10^{-1}	1.13×10^{-3}	−88 (± 9)	9.4
K	1.96×10^4	1.82×10^4	1.16×10^3	− 1 (± 1)	1.5
La	1.09×10^2	1.05×10^2	7.88	+ 4 (± 2)	1.0
Mg	6.23×10^4	5.54×10^4	6.75×10^3	0 (± 1)	2.1
Mn	1.68×10^3	1.45×10^3	1.88×10^2	− 2 (± 1)	1.6
Mo	4.05×10^1	3.71×10^1	4.13	+ 2 (± 1)	1.8
Na	2.21×10^3	2.03×10^3	1.46×10^2	− 2 (± 1)	1.8
Nb	7.48×10^1	7.09×10^1	3.75	0 (± 1)	1.7
Nd	1.96×10^2	1.72×10^2	2.03×10^1	− 2 (± 1)	2.0
Ni	7.48×10^1	7.09×10^1	4.50	+ 1 (± 1)	1.0
P	1.12×10^3	9.79×10^2	3.53	−12 (± 5)	2.1
Pb	6.86×10^1	5.74×10^1	9.38×10^{-1}	−15 (± 3)	5.9
Rb	2.74×10^2	2.63×10^2	8.25	− 1 (± 1)	1.2
S	1.84×10^5	7.76×10^4	1.54×10^3	−57 (± 6)	8.4
Sc	1.59×10^1	1.59×10^1	7.13×10^{-1}	+ 4 (± 1)	0.9
Se	7.48	6.08	1.39×10^{-1}	−17 (± 2)	7.9
Sm	1.22×10^1	1.18×10^1	3.30×10^{-1}	− 1 (± 1)	1.8
Sr	2.06×10^3	1.99×10^3	5.63×10^1	− 1 (± 1)	1.4
Tl	8.41×10^{-1}	7.43×10^{-1}	3.34×10^{-2}	− 8 (± 1)	3.1
V	2.77×10^2	3.11×10^2	9.00	+16 (± 4)	1.3
Y	9.97×10^1	9.19×10^1	1.16	− 1 (± 1)	1.5
Yb	9.04	8.78	7.50×10^{-2}	− 2 (± 1)	1.6
Zn	1.40×10^2	1.15×10^2	2.74	−16 (± 3)	4.1
Zr	2.87×10^2	3.21×10^2	9.00	+15 (± 3)	1.1

P.O.A. – Precipitator Outlet Ash

P.I.A. – Precipitator Inlet Ash

$\frac{\text{P.O.A.}}{\text{P.I.A.}}$ – Concentration ratios of the different fly ashes

Table 5: **Annual emissions due to brown-coal combustion of 1.14 x 10^8 t for power production in the Federal Republic of Germany.**
(After Heinrichs, 1982)

Element emission, t/yr			
As	8.5	Cl	2.9×10^4
Bi	0.23	F	3.3×10^3
Cd	0.39	P	2.0×10^2
Hg	4.5	S	1.6×10^5
Pb	15.		
Se	1.9		
Tl	0.10		
Zn	34.		

t/yr – Metric tons per year

balances was accomplished when the sum of the trace elements in the incoming streams equaled within statistical error limits the amount in all of the exit streams. Out of a total of eighty-one element material balances computed, sixty-five closed within + or - 35 % and another seven within + or - 50% . The material balances in Table 6 were represented as a ratio only:

total sum in outlet streams / total sum in inlet streams

The proportion of input material accounted for in the resulting mass balance for mercury ranged 13 to 212%. At one plant molybdenum resulting mass balance was 404 per cent. The authors feel the differences cannot simply be explained by the difficulty of recovering volatile elements from the gas phase. Comparing emission from two plants, with electrostatic precipitators on the hot side and on the cold side of the air heater, indicated that some of the volatile elements were not as completely condensed on the hot side as the cold. Also, that some trace elements were more concentrated in smaller particles than in larger ones. This enrichment of certain elements in the smaller size range, and the relative inefficiency of collection in this size range, explained the disproportionate atmospheric emissions of some elements. And aside from those elements such as sulfur and mercury, which are known to be present mostly in the vapor phase, the other flue gas enriched elements may exist in either the vaporous or condensed state and be emitted via the flue gas in higher proportions than the bulk fly ash.

Table 6: Trace element flows* and material balance results around station 1.
(After Meserole et al., 1979)

Element	Coal	Ash Sluice Water	Σ In	Bottom Ash	Bottom Ash Sluice Water	Economizer Ash	Economizer Ash Sluice Water	Cyclone Ash	Flue Gas South Duct	Flue Gas North Duct	Σ Out	Σ Out/ Σ In
Aluminium	1740	0.11	1740 ± 220	1480	.30	13.	.05	463	164	82	2200 ± 260	1.26
Antimony	.094	.0048	.10 ± .02	.013	.0061	.00008	.0018	.0049	.040	.025	.09 ± .01	.90
Arsenic	1.9	.0016	1.9 ± .3	.33	.0015	.019	.0001	1.2	.15	.25	1.9 ± .2	1.00
Barium	102	< .13	103 ± 23	96	< .089	1.3	< .044	48.	< 1.3	< 1.0	147 ± 26	1.43
Berryllium	.14	.0004	.14 ± .02	.089	.0003	.00014	.0003	.052	.0006	.004	.15 ± .02	1.07
Boron	36	.07	36 ± 5	8.7	.045	.11	.21	10.	16.	6.4	42 ± 3	1.17
Cadmium	.046	.00007	.046 ± .007	.015	.0002	.0003	.0001	.018	.012	.011	0.56 ± .005	1.22
Calcium	3220	9	3230 ± 330	2180	8.	18.	.4.	816.	397.	204.	3630 ± 340	1.12
Chlorine	13	3.2	16 ± 2	1.5	2.8	.02	1.5	.84	6.4	8.0	21 ± 2	1.31
Chromium	3.1	< .014	3.1 ± 4	1.6	.0094	.019	.0046	.54	.78	.68	3.6 ± .4	1.16
Cobalt	.18	.00007	.18 ± .02	.17	.0007	.0018	.0003	.081	.062	.039	.35 ± .03	1.94
Copper	2.5	.002	2.5 ± .4	.84	.002	.014	.0007	.90	.42	.20	2.5 ± .2	1.00
Fluorine	13.	.05	13 ± 2	< .17	.044	.01	.02	4.2	6.4	6.1	17 ± 2	1.31
Iron	1770	.11	1770 ± 210	1100	.4	10.	.12	358	2.08	103	1780 ± 180	1.01
Lead	.20	.0040	.21 ± .04	.013	.0043	.0013	.0022	.051	.062	.062	.20 ± .02	.95
Magnesium	870	7	880 ± 90	623	4.6	5.8	2.1	226	100	49	1010 ± 100	1.15
Manganese	18	.022	18. ± 2	12	.0098	.14	.0084	4.7	1.6	.8	19 ± 2	1.06
Mercury	.017	.0001	.017 ± .002	< .0002	< .00008	.00001	< .00004	.0011	.018	.016	.036 ± .004	2.12
Molybdenum	.46	.0087	4.7 ± .08	.30	.0028	.0068	.0010	.38	.46	.70	1.9 ± .2	4.04
Nickel	1.3	.0016	1.3 ± .2	.39	.0002	.0055	.0006	.24	.52	.56	1.7 ± .2	1.31
Selenium	.31	.0003	.31 ± .03	.0042	.0002	.00002	.0001	.059	.070	.049	.18 ± .01	.58
Silver	.0079	< .00006	.008 ± .001	.0018	.00004	.00004	< .00002	.00002	< .0007	< .0006	.0078 ± .0007	.98
Sulfur	3380	18	3400 ± 340	1.6	13.	.20	6.7	54.	1560	1390	3020 ± 300	.89
Titanium	82.	.027	82 ± 10	59	< .018	.59	< .0087	19.	3.4	3.3	85 ± 10	1.04
Uranium	.36	.0006	.36 ± .04	.054	.0006	.0017	.0004	.075	.034	.016	.18 ± .02	.50
Vanadium	3.5	< .0013	3.5 ± .5	2.4	< .0009	.017	< .0004	.54	.57	.41	3.9 ± .4	1.11
Zinc	1.8	.0034	1.8 ± .3	.30	.0023	.022	.0024	.75	.78	.41	2.3 ± .3	1.28

*All flow rates in lb/hr.

A thorough investigation to characterize the various waste streams by identifying the mass flow rates of the minor and trace elements in each waste stream, obtained mass balances for twenty-eight elements at the 200 MW(e) Tenessee Valley Authority's Kingston Steam Plant Unit 6 (Zielke and Bittman, 1982). The plant's inlet and outlet flows of the pulverizer, boiler, and electrostatic precipitator were extensively sampled. The sampling was divided into "two efforts": one focused on the gaseous and particulate emissions from the boiler and the other the different plant ashes. The mass balance range for the entire system was determined to be -12.5 to +6.3%. Many of the element mass imbalance exceeded + or - 12% (Table 7). The relative abundances of these element in whole coal are given in the rank column. It was noted that these "rankings and percentages depend only on the measured concentrations, not on estimated flows". Ten of the elements , Al, Be, Ca, Cr, Fe, Mg, S, Si, Ti and V, had imbalances of less than + or - 15% and they represented about 93% of the total fly ash and bottom ash mass flow rates. Large amounts of F, Cl, Hg, Se, Sb and Ag were not determined in the mass balance. The Ag in the sample was too small to analyze and the others were thought to be found in the gas at very low concentrations. It was concluded that sampling procedures needed to be improved for these elements.

Table 7: Balance of individual elements (After Zielke and Bittman, 1982)

Rank	Element	Balance (%)	Rank	Element	Balance (%)
4	Fe	103.7	21	Pb	82.6
1	Si	99.6	16	Cu	79.8
15	V	97.6	5	K	79.2
2	Al	96.5	22	As	77.3
25	Be	96.3	18	Zn	69.6
7	Ti	95.4	20	Co	65.8
3	S	94.2	28	Cd	65.1
8	Mg	92.5	13	B	62.8
17	Cr	91.7	23	Ag	36.1
6	Ca	90.2	26	Sb	31.8
19	Ni	89.7	24	Se	13.9
11	Ba	88.1	27	Hg	8.8
14	Mn	87.5	12	F	2.9
10	Na	84.4	9	Cl	0.6

At the 270 MW(e) Milliken Station coal-fired power plant in the state of New York, coal, bottom ash, and fly ash were analyzed for 20 elements, including the major natural radionuclides (Klusek et al., 1983). Mass balance calculations were computed using average trace element concentrations from samples of coal, fly ash, and bottom ash, and the calculated flow rate for each compartment. The imbalance was calculated as the ratio:

% imbalance = ((total output in ash - input in coal)/input in coal) X 100

The data in Table 8 indicated a + or - 25 % imbalance between input and output for 9 elements and that six of the elements had more of the element leaving the stream in the ash than entering via the coal. This disagreement was attributed to experimental error. The balances for Hg (-67 %), Sb (-64 %), and Se (-33%) indicated to the authors that the total in ash output was less than coal input. This suggested that some fraction of the unaccounted flow may be discharged into the environment through stack emissions.

A recent German mass balance study supports the "role of uncertainty of sampling, stream collection, and analysis" in the imprecise determination of trace element mass balances in coal-fired plants (Gerhard et al., 1985). The authors indicated that only a few trace element amounts in the coal were approximately accounted for in the slag, fly ash, flue-gas dust, and purified flue gas from the combustion of coal in three power plants.

4. Discussion of Literature: Overview of Problems in Mass Balance Determinations

Ideally, one should be able to calculate an exact balance of elements entering and leaving a steam plant, since the weight of each trace element that enters in the coal and the weight of each trace element that leaves in ash, slag, and gas should be able to be determined. The inability to accurately sample a facility, combined with poor analytical technique and the loss of some waste products, results in major inconsistencies and problems with mass balance measurements. These include the large element imbalances and the handling and interpretation of data to indirectly determine deposition or emission values of trace elements.

Previous mass balance studies have represented wide margins of error in many of the element balances. Serious positive and negative imbalances

Table 8: Trace element flow and percentage imbalance.
(After Klusek et al., 1983)

Element	Element Flow[a] (g/min)			% Imbalance[b]
	Coal	Fly Ash	Bottom ash	
Ag	0.25	0.22	< 0.003	− 12
Al, %	2.25	1.72	0.43	− 4
As	4.77	4.18	0.16	− 9
Be	0.48	0.57	0.22	65
Cd	0.11	0.08	0.01	− 18
Co	5.20	5.66	1.65	41
Cr	19.93	20.48	5.39	30
Cu	12.13	11.86	2.39	17
Ga	3.21	4.31	1.21	72
Hg	0.15	0.019	0.0002	− 87
Mn	17.33	23.72	6.06	72
Ni	16.47	13.88	3.07	3
Pb	8.67	8.22	0.22	− 3
Sb	1.13	0.31	0.10	− 64
Se	0.80	0.43	0.11	− 33
Sn	0.62	1.12	0.24	120
V	36.40	27.76	6.74	− 5
Zn	21.67	19.14	1.82	− 3

[a]Flow rates: coal = 866,686 g/min;
fly ash = 134,760 g/min;
bottom = 33,690 g/min.

[b]Imbalance = (bottom ash + fly ash − coal)/coal.

are noted for many of the elements as well as wide closures for computed values. Notable study closures are given as: within 30 % or less (Bolton et al., 1973); + or - 35 % for 65 elements and + or - 50 % for 7 elements (Meserole et al., 1979); and + or - 25 % for 9 elements (Klusek et al., 1983). The imbalances are excessive when considering any statistical precision or accuracy and the reproducibility of data.

It is important to note imbalance values depend on sampling procedure and accuracy. This can be seen by the formulas used to determine percent imbalance. Gas flow and/or trace element concentrations in the outlet streams were omitted in formulas if sampling was inadequate or not done on that fraction (Bolton et al., 1973; Klein et al., 1975; Heinrichs, 1982). This may be less than 1% difference in imbalance error because the outlet ash is a very small fraction of total ash, but the lack of proper measurement of the

more volatile elements has been found to provide excessive percent imbalances.

Most mass balance mesurements indirectly determine the discharge to the atmosphere of heavey metals and other toxic elements (Billings et al., 1973; Bolton et al., 1973; Kalb, 1973; Klein et al., 1975; Kaakinen et al., 1975; Zoller et al., 1975; Tadmor, 1986). It has been previously established that the wide + or - imbalances (Table 9) of elements As, B, Be, Bi, Br, Cd, Cl, Co, Cr, F, Hg, Pb, Sb, Se, Sn and Zn, indicate that these are the problematic elements. These elements are known to be volatile at combustion temperatures and found to concentrate in the smaller submicron particles or remain in the gas phase. In the recent study by Klusek et al. (1983), a relatively small amount of Hg was found to be retained in a coal-fired 270 MW(e) power plant. A plant imbalance of -87 % for Hg was determined. It was speculated that this imbalance indicated Hg may be released to the environment. This is in agreement with other investigators who maintained that poor mass balance closures suggested Hg exits partially as vapors in the flue gas. Comparible imbalances in Table 9 for Hg verify a consistent recovery problem of this volatile element. Whether these element imbalances determine total or partial discharge to the atmosphere of an element or accurate emission values has yet to be substantiated.

It is clear that large imbalances of volatile elements found in the literature reflects inadequate sampling technique and possible direct release into the environment as a vapor and/or as very fine particles. Numerous studies refer to the unsuccessful sampling and measurement of trace elements in the vapor and small particles in the flue gas (Kaakinen et al., 1975; Heinrichs, 1977, 1982; Meserole et al., 1979; Gerhard et al., 1985). The difficulty in sampling of volatile elements was demonstrated in the study by Klein et al. (1975). The impinger solutions for gas collection were not analyzed for either Cl or Br; as a result large negative percent imbalances for both elements were indicated. The study's large negative imbalances for arsenic in the impinger solutions was additional evidence of sampling inadequacies.

In-plant flow rates have not frequently been focused on as a possible concern in mass balance measurements. Flow rates of each stream or mass flows are mentioned as a requirement in mass balance calculations. But Zielke and Bittman (1982) proposed that drastic improvement of mass balance estimates could be obtained if the ability to measure flow rates

Table 9: Compariable imbalances for elements (%).

	Kaakinen and Jorden (1974)	Klein et al. (1975)	Klusek et al. (1983)	Zielke and Bittman (1982)	Heinrichs (1982)
As	+ 46	+ 43 − 57	− 9	− 23	− 13
Be			+ 65		− 5
Bi					− 27
Br		− 90		− 4	
Cd		+ 24	− 18	− 34	− 23
Cl		− 98		− 99	− 94
Cr		+ 28 + 33	+ 30	− 8	
Co		− 2 + 9	+ 41	− 34	+ 4
F				− 97	− 74
Hg	− 90	− 97	− 87	− 91	− 88
Pb		− 9 − 11	− 3	− 17	− 15
Sb		+ 27	− 64	− 68	
Se	+ 62	− 22	− 33	− 86	− 17
Sn	+ 88		+ 120		
Zn	+ 55	− 35	− 3	− 30	− 16

around the boiler improved, and recommended a longer sampling program "to help quantify the time dependencies of power plant data," because of the variability in power plant operating conditions including the flow rates.

In the final analysis, the real problem is the inability to initially determine accurate data values because of poor sampling technique. A more representative sampling would alleviate partially the errors in balance determinations, especially if improvement was in the sampling of vapors and the submicron size fly ash. The improvement in the determination of initial concentrations in the outlet streams could improve such predictive

calculation approaches like that of Tadmore (1986) and his use of mass balance data to calculate the percentages of radioelements in phases other than the ash, and the future predictions of trace element emission values in particulates and vapors of coal-fired facilities.

5. Improvement of Mass Balance Measurements

Experimental coal combustion systems have afforded mass balances that are generally more accurate than in-plant measurements. This indicates that vast improvement of mass balance measurement is possible in coal-fired power plants with improved technology.

The measurement of 24 trace and minor elements in the feed and exit streams was conducted using an experimental 2.25 sq. ft. atmospheric fluidized-bed combustor (Hall et al., 1982). Material balance closures for Ca, Mg, Mn, V and Zn were in 90 to 110 % range. The total element ranges for 16 elements had average balance closures of 93 % of respective imputs, and only 8 elements were below 90 %. This is an improvement over power plant measurements of the trace elements listed in Tables 1 and 9. In Quann et al. (1982) the efficiency of collection of the submicron fraction in a laboratory pulverized coal high temperature combustion system was tested by performing a material balance on selected elements. Generally, more than 90% of an element in the coal feed was recovered in the particulate product, which indicated no significant loss of particulate or inorganic vapor material within the furnace, collection probe, or modified impactor head.

It is apparent to effectively improve mass balance measurements in coal-fired plants laboratory experimental systems should be developed that are concerned with the precise sampling of the more deceptive trace elements that concentrate in the submicron fraction and gases. The laboratory development and improvement of sampling apparatus would afford better in-plant collection systems as well as give information where certain trace elements may be expected to concentrate during certain combustion conditions. A better understanding of the mechanisms of release to the environment would also be obtained. As of yet, there has not been enough research of this type done. The current sampling techniques and problems are discussed in the following sections.

6. Trace Element Enrichment Studies Reviewed

In the last section a review of the trace element mass balance investigations in coal-fired plants determined that improvement of measurement is needed to provide a concise data base in which to compare facilities. However, the investigations in the literature on trace elements in coal-fired plants generally have been more concerned with the determination of enrichment trends of trace elements in ash fractions and/or size particles than overall mass balance measurements. These types of studies can eventually improve sampling and analytical techniques of trace elements and the data used in mass balance determinations. Presently, there is still considerable need in improvement in both enrichment trends and mass balance assessments. In order to have a true understanding of trace element research in coal-fired facilities the two types of trace element enrichment studies must be defined and reviewed.

6.1 Trace Element Enrichment in Ash Fractions

Enrichment trend determinations are of two types. They are either trace element distribution in the different ash streams, such as the bottom ash, electrostatic precipitator ash and stack emissions, or distribution according to particle size, especially the measurement of increase in concentration with decrease in particle size of the finer particulates. Trace element concentrations in the different ash fractions are described as partitioning behavior in a coal-fired plant. Partitioning behavior in coal-fired facilities has been investigated by Klein et al. (1975) and Meij et al. (1986). The trace element concentration patterns of these two studies are in relatively good agreement, considering differences in plant operating conditions and the dates of the studies. Trace element distribution differences in coal-fired plants can result from the temperature of firing, precipitator efficiencies, and coal types. These two studies reflect the basic approach of partitioning investigations and are discussed here.

In the study by Klein et al. (1975), increased concentrations of certain trace elements were found in the fly ash relative to the slag (or bottom ash) and in the ash discharged through the stack relative to the ash collected by the precipitator (Table 10). Both Klein et al. (1975) and Meij et al. (1986) indicated the enrichment of the fly ash in certain trace elements and the loss of volatiles by trace element concentration ratios or enrichment factors. In Klein et al. (1975), ratios were given that reflected the

Table 10: Concentrations and concentration ratios. (After Klein et al., 1975)

	Element concentration, ppm				Concentration ratios		
	Coal	Slag	Inlet fly ash	Outlet fly ash	Slag/coal	(Inlet fly ash)/slag	(Outlet fly ash)/(inlet fly ash)
Al	10,440	102,300	90,900	76,000	9.8	0.9	0.8
As	4.45	18	110	440	3.6	6.1	4.0
Ba	65	500	465	750	7.7	0.9	1.6
Br	3.7	2	~ 4		0.5	2.0	
Ca	4,340	46,000	25,200	32,000	10.6	0.5	1.3
Cd	0.47	1.1	8.0	51	2.3	7.3	6.4
Ce	8.2	84	84	120	10.2	1.0	1.4
Cl	914	≤ 100	≤ 200		≤ 0.1	~ 1	
Co	2.9	20.8	39	65	7.2	1.9	1.7
Cr	18	152	300	900	8.4	2.0	3.0
Cs	1.1	7.7	13	27	7.0	1.7	2.1
Cu	8.3	20	140		2.4	7.0	
Eu	0.1	1.1	1.3	1.3	11.0	1.2	1.0
Fe	10,850	112,000	121,000	150,000	10.3	1.1	1.2
Ga	4.5	5	81		1.1	16.2	
Hf	0.4	4.6	4.1	5.0	11.5	0.9	1.2
Hg	0.122	0.028	0.050		0.2	1.8	
K	1,540	15,800	20,000	24,000	10.3	1.3	1.2
La	3.8	42	40	42	11.0	1.0	1.0
Mg	1,210	12,400	10,600		10.2	0.9	
Mn	33.8	295	298	430	8.7	1.0	1.4
Na	696	5,000	10,100	11,300	7.2	2.0	1.1
Ni	16	85	207		5.3	2.5	
Pb	4.9	6.2	80	650	1.3	12.9	8.1
Rb	15.5	102	155	190	6.6	1.5	1.2
Sb	0.5	0.64	12	55	1.3	18.8	4.6
Sc	2.2	20.8	26	36	9.5	1.2	1.4
Se	2.2	.080	25	88	0.0	310	3.5
Si	23,100	229,000	196,000		9.9	0.9	
Sm	1.0	8.2	10.5	9	8.2	1.3	0.9
Sr	23	170	250		7.4	1.5	
Ta	0.11	0.95	1.4	1.8	8.6	1.5	1.3
Th	2.1	15	20	26	7.1	1.3	1.3
Ti	506	4,100	5,980	10,000	8.1	1.5	1.7
U	2.18	14.9	30.1		6.8	2.0	
V	28.5	260	440	1,180	9.1	1.7	2.7
Zn	46	100	740	5,900	2.2	7.4	8.0

partitioning behavior in the various ash streams and grouped them into three classes (Table 11). The ratios are as follows:

Slag/coal, Inlet fly ash/Slag, Outlet fly ash/ Inlet fly ash

These concentration ratios evolved the three classes of partitioning behavior:

Class I: slag/coal $\geq$ 6.6, (inlet fly ash)/slag = 1.2, S =0.3,

outlet fly ash/inlet fly ash = 1.3, S = 0.5

S = standard deviation

Elements are readily incorporated into the slag and are partitioned about equally between the inlet fly ash and slag. There is no apparent tendency to concentrate in the outlet fly ash.

Class II: slag/coal $\leq$ 3.6, (inlet fly ash)/slag = > 6,

outlet fly ash/inlet fly ash = $\geq$ 3.5

Elements are poorly incorporated into slag and are concentrated in inlet fly ash compared to slag and in the outlet fly ash compared to the inlet fly ash.

Class III: Elements remain almost completely in the gas phase.

In contrast, Meij et al. (1986) investigated the degree of enrichment of trace elements in the fly ash due to evaporation and condensation. Fly ash was defined as the stack emitted portion of the pulverized-coal ash that was not caught by electrostatic filters. The relative enrichment factor (RE) was applied to indicate the degree of enrichment of trace elements in the fly ash due to the evaporation and condensation mechanism.

$$RE = \frac{\text{element concentration in ash}}{\text{element concentration in coal}} \cdot \frac{\% \text{ coal ash}}{100}$$

Table 11: Classes of trace element partitioning reported by Klein et al. (1975) and Meij et al. (1986)

Klein et al. (1975)	Meij et al. (1986)
Class I Al, Ba, Ca, Ce, Co, Eu, Fe, Hf, K, La, Mg, Mn, Rb, Sc, Si, Sm, Sr, Ta, Th, Ti.	Al, Ce, Cr, Cs, Eu, Fe, Hf, K, La, Rb, Sc, Si, Th, Ti.
Class II As, Cd, Cu, Ga, Pb, Sb, Se, Zn.	IIa: As, Cs, P, Pb, Sb, Se, W, Zn. IIb: Be, Co, Cu, Mg, Mn, Mo, Ni, U, V, Sr. IIc: Ba, Ca, Na, Sm.
Class III Hg, Cl, Br.	B, Br, Cl, F, Hg.
Cr, Cs, Na, Ni, U, and V appeared to be intermediate between Classes I and II.	Be, Ca, Mg, Mn, Na and Sr have been placed in class II contrary to the literature. Be and Sr were depleted in bottom ashes. Ca, Mg, Na, and Sm were not. Ca and Mn were enriched in bottom ash.

Computed enrichment factors are frequently used in the literature to represent trace element enrichment or loss in the ash or gas phase and to describe partitioning in the various ash streams (Kaakinen et al., 1975; Weissman et al., 1983; Conzemius et al., 1984). The RE factor was used in this study to group elements into classes with different volatilizations. The following classes were differentiated as a result of the enrichment factors.

Class I ($0.7 < RE < 1.3$): Elements are mostly not volatile and have no significant additional enrichment in the emitted fly ash.

Class II ($RE > 1.3$ and $RE < 0.7$): Elements are enriched in emitted fly ash ($RE > 1.3$) and depleted in bottom ash ($RE < 0.7$).

Three subgroups of Class II are distinguished :

IIa: $RE > 4$

IIb: $2 < RE \leq 4$

IIc: $1.3 < RE \leq 2$

Class III ($RE << 1$): Elements that escape mostly as gases.

Meij et al. (1986) does not agree that Cr, Cs, Na, Ni, U and V showed irregular behavior between class I and II but placed Cr and Cs in class I and further subdivided the classification scheme to include 3 subclasses of class II (Table 11). It is important to note that for both studies the relationship between the enrichment factor or concentration ratios and the ash particle size is observed as an increase in class II elements with decreased particle size. Most class II trace elements are highly enriched in the fly ash and fume in the colder parts of an installation.

In a study done by Conzemius et al. (1984), the data also showed excellent agreement that class II elements have a tendency to partition in a plant. They used the same classification defined by Klein et al. (1975). The class II elements, As, Cd, Ga, Ge, Pb, Sb, Sn, Tl and Zn, were highest in the electrostatic precipitator ash relative to the Bottom ash and primary mechanical collector ash. The elements Ge, Sn and Tl were not determined by either Klein et al. (1975) or Meij et al. (1986). A plot of the computed enrichment factors for the class II elements is given in Figure 1. Similar behavior is observed among this group of elements. Pb and Cd do have the greatest range of partitioning for both the coal types tested and Sn is significantly less partitioned in the Iowa coal. The enrichment factors (Table 12) indicated partitioning behavior that was intermediate between the class I and class II elements for 10 elements: Bi, Cs, Cu, I, Mo, Na, Se, Ta and W. This is not entirely consistent with the results of Klein et al. (1975) and Meij et al. (1986), in which only Cs and Na are considered as intermediate (Table 13). Most of the other elements that were studied fell into class I showing no partitioning. The elements Mn, Ca, Fe and Si for the Iowa coal and Fe for the Colorado coal were indicated as having small depletions at the ESP site.

It is clear from the above survey that the investigations of partitioning of trace elements in coal-fired facilities have determined that trace

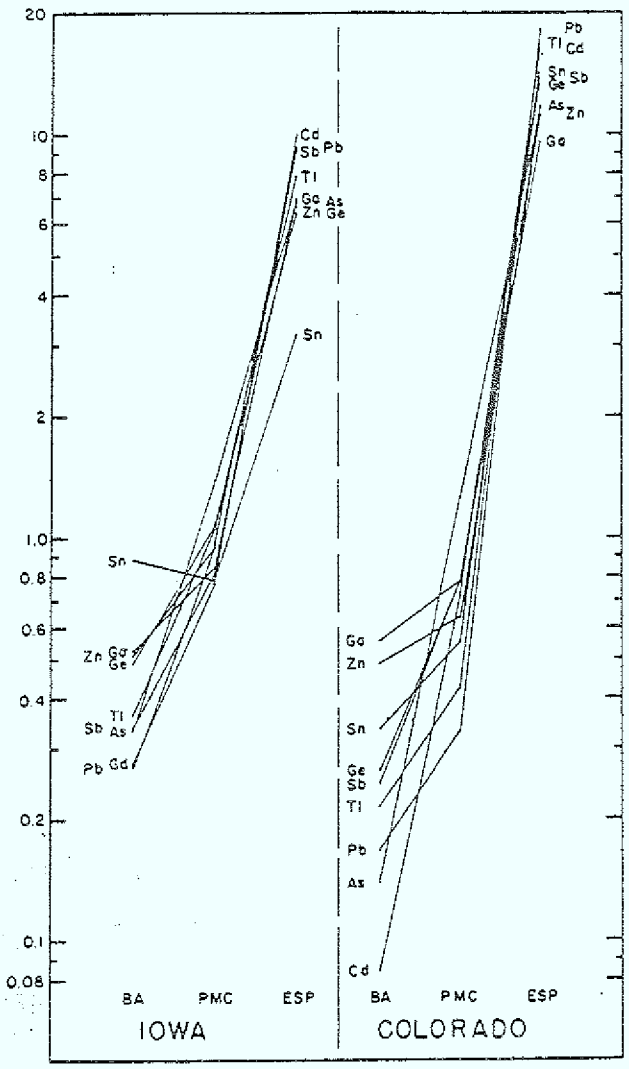

Figure 1: Plot of enrichment factors for elements partitioned in the ashes. (After Conzemius et al., 1984)

elements do tend to concentrate in the smaller ash fractions. The use of enrichment factors, calculated from trace element concentrations in the various ash fractions, reflects the partitioning of particular trace elements. Enrichment factors and concentration ratios evolve classes of partitioning behavior that describe not only partitioning in the ash but volatization behavior. It is indicated that class II trace elements increase with decreased particle size.

Investigating the increase in concentration with decrease in particle size and determining any variations as a function of particle size, is the strategy of most trace element enrichment studies. Before the concentration -

Table 12: Enrichment Factors* by SSMS in Three Ash Depositories for an Iowa Coal and a Colorado Coal. (After Conzemius et al., 1984)

Iowa coal					Colorado coal				
no.	Sy	BA	PMC	ESP	no.	Sy	BA	PMC	ESP
1	Cd	0.28 ± 0.10	0.77 ± 0.21	9.99 ± 2.71	1	Pb	0.17 ± 0.06	0.33 ± 0.11	18.13 ± 5.79
2	Pb	0.27 ± 0.08	0.96 ± 0.24	9.27 ± 2.33	2	Tl	0.21 ± 0.07	0.42 ± 0.13	16.75 ± 4.91
3	Sb	0.34 ± 0.09	0.83 ± 0.21	9.04 ± 2.25	3	Cd	0.08 ± 0.03	0.73 ± 0.23	16.36 ± 4.68
4	Tl	0.37 ± 0.14	1.06 ± 0.26	7.87 ± 1.95	4	Sn	0.33 ± 0.10	0.55 ± 0.15	14.09 ± 3.67
5	Ga	0.52 ± 0.14	0.85 ± 0.20	6.92 ± 1.57	5	Sb	0.24 ± 0.07	0.77 ± 0.21	13.70 ± 3.51
6	As	0.34 ± 0.09	1.39 ± 0.32	6.79 ± 1.58	6	Ge	0.26 ± 0.07	0.78 ± 0.21	13.35 ± 3.35
7	Zn	0.51 ± 0.17	0.95 ± 0.26	6.64 ± 1.58	7	As	0.14 ± 0.04	1.25 ± 0.42	11.66 ± 2.95
8	Ge	0.49 ± 0.12	1.08 ± 0.23	6.34 ± 1.36	8	Zn	0.49 ± 0.19	0.63 ± 0.19	11.24 ± 3.29
9	Sn	0.88 ± 0.23	0.78 ± 0.17	3.19 ± 0.72	9	Ga	0.56 ± 0.14	0.78 ± 0.17	9.10 ± 1.94
10	Mo	0.77 ± 0.19	1.19 ± 0.25	2.84 ± 0.59	10	Bi	≦ 0.74	≦ 0.61	≧ 7.9
11	Cu	0.88 ± 0.20	0.89 ± 0.18	2.78 ± 0.55	11	I	0.27 ± 0.07	1.89 ± 0.44	4.87 ± 0.99
12	Bi	≦ 0.85	≦ 1.01	≧ 2.67	12	Hf	0.74 ± 0.24	1.00 ± 0.28	4.70 ± 3.99
13	Cs	0.79 ± 0.21	1.19 ± 0.33	2.54 ± 0.62	13	Na	0.79 ± 0.21	0.94 ± 0.20	4.56 ± 0.95
14	I	0.57 ± 0.15	1.88 ± 0.41	2.25 ± 0.47	14	Mo	0.87 ± 0.20	0.83 ± 0.18	4.15 ± 0.81
15	Co	0.80 ± 0.18	1.27 ± 0.25	2.15 ± 0.42	15	F	0.55 ± 0.14	1.48 ± 0.37	3.94 ± 0.87
16	V	0.84 ± 0.19	1.20 ± 0.25	1.95 ± 0.40	16	Cl	0.75 ± 0.19	1.15 ± 0.27	3.50 ± 0.96
17	Se	1.05 ± 0.27	0.65 ± 0.15	1.89 ± 0.41	17	Dy	0.69 ± 0.19	1.31 ± 0.35	3.25 ± 0.69
18	Ta	0.96 ± 0.21	0.89 ± 0.20	1.84 ± 0.49	18	Ta	1.04 ± 0.33	0.63 ± 0.17	3.19 ± 0.95
19	Na	1.04 ± 0.25	0.70 ± 0.15	1.78 ± 0.46	19	Cu	1.05 ± 0.24	0.61 ± 0.13	3.15 ± 0.61
20	Nd	0.85 ± 0.20	1.24 ± 0.25	1.70 ± 0.34	20	Cs	0.90 ± 0.26	0.93 ± 0.25	2.91 ± 0.73
21	U	0.84 ± 0.21	1.28 ± 0.27	1.67 ± 0.34	21	Er	0.73 ± 0.19	1.27 ± 0.31	2.89 ± 0.61
22	Ni	0.97 ± 0.24	0.91 ± 0.20	1.65 ± 0.36	22	Se	1.05 ± 0.25	0.66 ± 0.15	2.84 ± 0.57
23	W	0.90 ± 0.36	1.12 ± 0.34	1.64 ± 0.48	23	W	1.05 ± 0.32	0.66 ± 0.18	2.80 ± 0.67
24	Yb	0.81 ± 0.19	1.39 ± 0.35	1.62 ± 0.35	24	U	0.67 ± 0.16	1.41 ± 0.29	2.76 ± 0.55
25	Sm	0.85 ± 0.23	1.28 ± 0.30	1.60 ± 0.34	25	Sm	0.71 ± 0.20	1.35 ± 0.34	2.67 ± 0.54
26	Ce	0.85 ± 0.20	1.28 ± 0.27	1.55 ± 0.34	26	Zr	0.87 ± 0.21	1.04 ± 0.21	2.59 ± 0.50
27	Dy	0.89 ± 0.29	1.17 ± 0.29	1.52 ± 0.37	27	Hg	0.99 ± 0.29	0.81 ± 0.32	2.56 ± 0.68
28	Er	0.85 ± 0.22	1.30 ± 0.28	1.50 ± 0.36	28	Gd	0.75 ± 0.20	1.29 ± 0.32	2.50 ± 0.51
29	Cl	0.73 ± 0.18	1.66 ± 0.42	1.45 ± 0.40	29	Sr	0.71 ± 0.20	1.37 ± 0.32	2.45 ± 0.50
30	Pr	0.93 ± 0.23	1.10 ± 0.25	1.44 ± 0.31	30	B	0.67 ± 0.19	1.45 ± 0.55	2.38 ± 0.58
31	F	0.83 ± 0.28	1.38 ± 0.40	1.41 ± 0.38	31	Ho	0.83 ± 0.18	1.15 ± 0.24	2.36 ± 0.47
32	Y	0.96 ± 0.21	1.02 ± 0.21	1.41 ± 0.29	32	Nd	0.89 ± 0.22	1.04 ± 0.24	2.28 ± 0.45
33	Mg	1.01 ± 0.24	0.87 ± 0.18	139 ± 0.28	33	Rb	0.98 ± 0.26	0.87 ± 0.22	2.28 ± 0.50
34	Gd	0.84 ± 0.23	1.36 ± 0.30	1.36 ± 0.30	34	Co	1.02 ± 0.23	0.81 ± 0.17	2.22 ± 0.43
35	Sr	1.01 ± 0.26	0.88 ± 0.19	1.34 ± 0.30	35	Yb	0.72 ± 0.19	1.40 ± 0.38	2.13 ± 0.51
36	Ba	1.01 ± 0.26	0.89 ± 0.19	1.29 ± 0.29	36	Tb	0.79 ± 0.18	1.28 ± 0.28	1.99 ± 0.40
37	La	0.91 ± 0.23	1.18 ± 0.26	1.27 ± 0.27	37	Eu	0.79 ± 0.19	1.27 ± 0.30	1.98 ± 0.39
38	Sc	0.93 ± 0.24	1.13 ± 0.24	1.26 ± 0.28	38	Tm	0.86 ± 0.22	1.16 ± 0.26	1.94 ± 0.48
39	S	1.16 ± 0.38	0.50 ± 0.14	1.25 ± 0.39	39	Ba	0.69 ± 0.19	1.48 ± 0.40	1.93 ± 0.51
40	Ti	0.86 ± 0.19	1.35 ± 0.26	1.20 ± 0.24	40	Cr	0.91 ± 0.23	1.04 ± 0.22	1.93 ± 0.43
41	Tm	0.89 ± 0.31	1.27 ± 0.38	1.15 ± 0.30	41	Ni	1.00 ± 0.23	0.89 ± 0.19	1.91 ± 0.39
42	Rb	0.90 ± 0.22	1.26 ± 0.31	1.07 ± 0.24	42	Ce	0.81 ± 0.19	1.24 ± 0.34	1.88 ± 0.38
43	Zr	0.91 ± 0.21	1.24 ± 0.25	1.07 ± 0.22	43	La	0.85 ± 0.22	1.20 ± 0.27	1.73 ± 0.36
44	Al	1.00 ± 0.26	1.00 ± 0.22	1.00 ± 0.21	44	V	0.91 ± 0.23	1.07 ± 0.25	1.73 ± 0.35
45	Hf	0.78 ± 0.22	1.61 ± 0.46	1.00 ± 0.27	45	Br	1.08 ± 0.36	0.75 ± 0.20	1.70 ± 0.50
46	P	0.95 ± 0.22	1.16 ± 0.25	0.96 ± 0.20	46	Pr	0.89 ± 0.21	1.14 ± 0.30	1.58 ± 0.34
47	Lu	0.93 ± 0.31	1.20 ± 0.31	0.95 ± 0.23	47	Lu	0.55 ± 0.19	1.80 ± 0.43	1.58 ± 0.40
48	Cr	0.92 ± 0.22	1.26 ± 0.27	0.92 ± 0.19	48	P	1.06 ± 0.27	0.82 ± 0.18	1.56 ± 0.32
49	Li	0.92 ± 0.27	1.26 ± 0.40	0.88 ± 0.27	49	Ti	1.15 ± 0.28	0.63 ± 0.14	1.56 ± 0.31
50	K	0.84 ± 0.19	1.47 ± 0.30	0.87 ± 0.17	50	Li	1.04 ± 0.33	0.86 ± 0.30	1.45 ± 0.38
51	B	0.96 ± 0.28	1.15 ± 0.29	0.84 ± 0.20	51	Mg	1.03 ± 0.24	0.88 ± 0.19	1.42 ± 0.28
52	Hg	1.15 ± 0.39	0.62 ± 0.37	0.82 ± 0.24	52	S	1.37 ± 0.43	0.23 ± 0.06	1.41 ± 0.42
53	Be	1.09 ± 0.46	0.78 ± 0.38	0.82 ± 0.39	53	Sc	0.96 ± 0.24	1.04 ± 0.24	1.33 ± 0.28
54	Ho	0.89 ± 0.22	1.37 ± 0.29	0.81 ± 0.18	54	K	1.03 ± 0.26	0.89 ± 0.21	1.33 ± 0.30
55	Eu	0.95 ± 0.26	1.20 ± 0.27	0.79 ± 0.19	55	Y	0.89 ± 0.22	1.18 ± 0.24	1.23 ± 0.25
56	Th	1.02 ± 0.26	1.00 ± 0.22	0.75 ± 0.17	56	Ca	1.08 ± 0.27	0.83 ± 0.18	1.14 ± 0.23
57	Tb	0.89 ± 0.22	1.38 ± 0.29	0.68 ± 0.14	57	Al	1.00 ± 0.26	1.00 ± 0.22	1.00 ± 0.20
58	Br	1.01 ± 0.34	1.07 ± 0.27	0.61 ± 0.16	58	Si	0.96 ± 0.22	1.08 ± 0.22	0.96 ± 0.18
59	Si	0.89 ± 0.20	1.45 ± 0.28	0.47 ± 0.09	59	Th	0.96 ± 0.24	1.09 ± 0.23	0.91 ± 0.19
60	Fe	1.14 ± 0.27	0.76 ± 0.16	0.45 ± 0.09	60	Mn	1.02 ± 0.25	0.99 ± 0.21	0.74 ± 0.15
61	Ca	1.11 ± 0.26	0.87 ± 0.18	0.32 ± 0.07	61	Be	1.34 ± 0.44	0.40 ± 0.14	0.62 ± 0.26
62	Mn	1.11 ± 0.26	0.90 ± 0.19	0.14 ± 0.03	62	Fe	1.15 ± 0.26	0.80 ± 0.17	0.29 ± 0.06

* Elements are listed in order of enrichment factor at the ESP site for each coal.

SSMS – Spark Source Mass Spectrometry
BA – Bottom Ash
PMC – Primary Mechanical Collector
ESP – Electrostatic Precipitator

Table 13: Comparison of trace element classifications reported by Klein et al. (1975), Conzemius et al. (1984) and Meij et al. (1986).

Elements*	Klein et al. (1975)	Meij et al. (1986)
Bi	not determined	not determined
Cs	intermediate	class I
Cu	class II	class II b
I	not determined	not determined
Mo	not determined	class II b
Na	intermediate	class II c
Se	class II	class II a
Ta	not determined	not determined
W	not determined	not determined

*Trace elements all intermediate between class I and II for Conzemius et al. (1984)

particle size relationship can be reviewed, it is important to examine in more detail the mechanism of fine particle enrichment and discuss the implications of the submicron fraction of ash.

6.2 Mechanism of Fine Particle Enrichment

The enrichment of trace elements on the surface of relatively small particles has brought forth a unique but highly plausible mechanism of enrichment theory. The concentrating of these elements is thought to be due to a vaporization - condensation mechanism that the different elements experience as a result of high temperatures in the boiler and ducts of a coal-fired plant. Volatization occurs during combustion and is then followed by condensation or adsorption over the available fly ash matrix material (composed of the nonvolatile oxides of Al, Mg, and Si) (Davison et al.,1974). Enrichment is thought not only to be produced by ash vapors depositing on the surface of residual ash particle but also through the nucleation of the vapors to form very small new particles (Taylor and Flagan, 1982). The smaller the particle the greater the surface area available to adsorb both volatile

inorganic and organic toxic compounds. These toxic fine particles can pass through a plant's particulate emissions control device and reside in the atmosphere thus increasing their chances of being inhaled by humans. The enrichment of trace elements on smaller particles has been described in other investigations (Natusch and Wallace, 1974; Natusch et al., 1974; Kaakinen et al., 1975; Klein et al., 1975; Lindberg et al. 1975; Ragaini and Ondov 1975; Ondov et al., 1978; Smith et al., 1980.

6.3 The Submicron Fraction

It has been determined by various researchers that the distribution of suspended particles in coal-fired burning is bimodal with distinct modes in a submicron and supermicron size ranges (Ragaini and Ondov, 1977; Ondov et al., 1979; Johnson et. al., 1982; Taylor and Flagan, 1982; Markowski and Filby, 1985). Research has concentrated on the larger mode as a result of the lack of sampling expertise. Quantitative measurements of the compostion of the larger mode from coal-fired utility boilers are thought to consist primarily of ash residue which remains after the carbon matrix is fully burned (Flagan and Friedlander, 1978). The submicron fraction is smaller than the larger mode and defined as particles with less than 1um aerodynamic diameters (Taylor and Flagan, 1982). Aerodynamic diameter of a particle is defined as "the physical diameter of a unit density sphere which settles through the air with a velocity equal to the particle in question" (Sem, 1984). The composition of the submicron fraction, sometimes referred to as ash aerosol, is highly variable due to the different coal-combustion operating conditions with temperature variation being highly determinant (Taylor and Flagan, 1982). Different facilities produce variations in temperature of the burning char particles and vaporization rates. These in turn influence the composition of the gas surrounding the char or ash particles and composition of the resulting combustion product. (Taylor and Flagan, 1982; Markowski et al., 1980; Weissman et al., 1983). It has also been observed that the composition of the ash particles smaller than 0.1 um diameter may differ substantially from other larger submicron particles and the variation can be seen from one combustion operating condition to another (Taylor and Flagan, 1980). It is apparent that a number of factors influence the resulting composition and quantities of the very small ash particles generated during the combustion of pulverized coal.

One study (Smith et al., 1979) in particular should be mentioned because the findings are contradictory to the predictions of most researchers that

the less than 1 um diameter particles concentrate trace elements. The results are not typical in that the concentrations of the volatile elements in the fly ash are nearly independent of particle size below approximately 1um diameter (Figure 2). The bursting of larger particles during rapid gas release followed by coagulation of much smaller fragments was the proposed mechanism for formation of submicron particles. The condensation of volatilized material may occur during and after coagulation. The authors did point out that while their results suggested that the concentration becomes independent of particle size for particles smaller than a few microns, they did not expect similar concentration profiles from all coal-fired plants. Lower temperatures or differences in mineral matter composition may make the busting mechanism unimportent in other coal-fired plants. It must also be mentioned that submicron particles were sampled from the electrostatic precipitator and not collected in-stack where most submicron particle sampling is performed. There is really little evidence to suggest that busting is the major mechanism of fine particle formation in coal combustion. The extreme variability of the composition of small ash particles produced from a single coal type under varied combusiton conditions and the formation of some particles which are devoid of the major ash constituents suggest that the vaporization-condensation mechanism dominates (Taylor and Flagan, 1982).

6.4 Trace Element Enrichment as a Function of Particle Size

The evaluation of the literature on trace element composition in fly ash as a function of particle size has demonstrated that there are increases in certain trace elements in smaller fractionated particles. Trace elements are separated into groups that are based on their tendency to enrich in smaller size particles. But consistent trends in trace element enrichment in smaller particles are not always found with similar studies reviewed.
The following studies provided evidence for the concentrating of many trace elements in increasing smaller particles.

Coles et al. (1979) measured concentrations and distributions according to four particle sizes of 42 minor and trace elements collected in-stack at a western coal-fired power plant. Mass median diameters of the particles were 2.4, 3.7, 6.0 and 18.5 um, larger than the previously defined submicron fraction. The particles were sized using a specially designed fractionator (McFarland et al., 1977). Findings determined that the fly ash concentrated

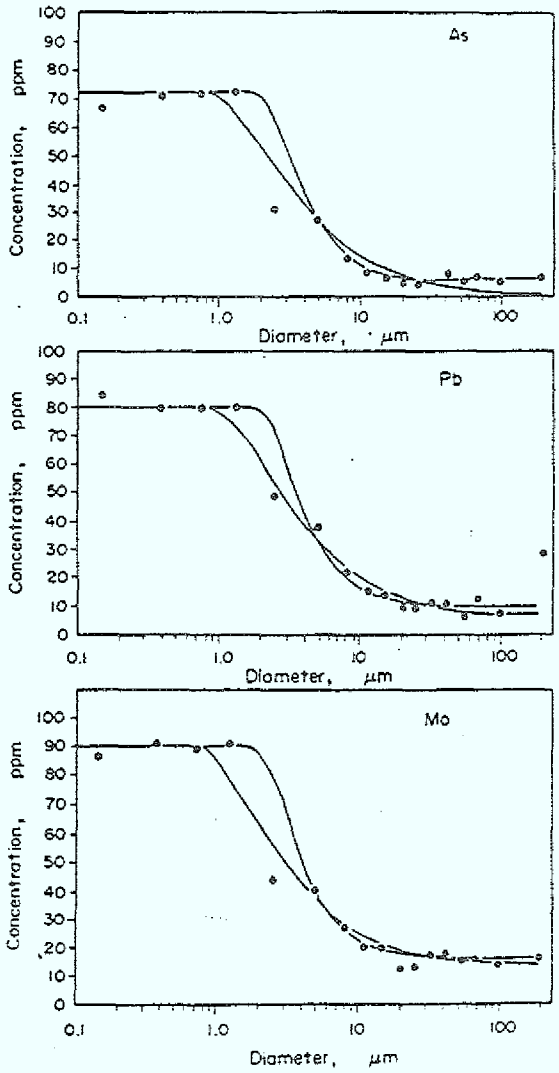

Figure 2: Average Concentration vs particle size profiles for three elements apparently volatilized during combustion. (After Smith et al., 1979)

As, Cd, Ga, Mo, Pb, Sb, Se, W and Zn with decreasing particle size (Table 14). The elements were grouped into three classes (Table 15) based on enrichment relative to coal as a function of fly-ash particle size from which the enrichment factor (EF) in each size fraction was calculated. Unlike the classes in the previous section which represent partitioning of the elements in total ash fractions, this classification is based on partitioning of elements in size particles that are called groups. Sampling for this type of study is usually collected totally from a precipitator or in-stack emissions.

Table 14: Comparison of elemental concentration in size-classified fly-ash fractions. (after Coles et al., 1979)

A. INAA and AAS[a]

Element	Concentration, µg/g (unless % indicated)			
	Fraction 1 18.5 µm[b]	Fraction 2 6.0 µm[b]	Fraction 3 3.7 µm[b]	Fraction 4 2.4 µm[b]
Al (%)	13.8 ± 0.1	14.4 ± 0.1	13.3 ± 0.6	13.9 ± 0.3
Ba (%)	0.168 ± 0.001	0.245 ± 0.002	0.31 ± 0.01	0.41 ± 0.02
Ca (%)	2.1 ± 0.1	2.23 ± 0.08	2.30 ± 0.14	2.36 ± 0.09
Co	8.9 ± 0.2	17.7 ± 0.4	20.3 ± 0.7	21.8 ± 0.4
Cr	28 ± 3	53 ± 3	64 ± 3	68 ± 3
Fe (%)	2.51 ± 0.09	3.09 ± 0.02	3.04 ± 0.08	3.2 ± 0.1
K (%)	0.74 ± 0.01	0.80 ± 0.07	0.82 ± 0.08	0.81 ± 0.03
Mn	208 ± 5	231 ± 5	269 ± 6	309 ± 5
Na (%)	1.22 ± 0.03	1.75 ± 0.05	1.81 ± 0.06	1.85 ± 0.03
Ni	25 ± 3	37 ± 1	43 ± 4	40 ± 2
Ti (%)	0.62 ± 0.05	0.74 ± 0.05	0.73 ± 0.1	0.77 ± 0.05
Zn	68 ± 1	189 ± 4	301 ± 9	590 ± 98

B. AAS only[c]

Be	6.3 (0.2)	8.5 (0.2)	9.5 (0.3)	10.3 (0.5)
Cu	56 (1)	89 (1)	107 (4)	137 (1)
Cd	0.4 (0.2)	1.6 (0.3)	2.8 (0.4)	4.6 (0.2)
Mg (%)	0.47 (0.01)	0.56 (0.01)	0.60 (0.02)	0.63 (0.01)
Pb	73 (3)	169 (2)	226 (4)	278 (3)
Si (%)	29.6 (0.7)	28.0 (0.1)	27.5 (0.3)	26.8 (0.1)

C. INAA[d] Only

Element	Concentration, µg/g (unless % indicated)			
	Fraction 1 18.5 µm[b]	Fraction 2 6.0 µm[b]	Fraction 3 3.7 µm[b]	Fraction 4 2.4 µm[b]
As	13.7 ± 1.3	56 ± 14	87 ± 9	132 ± 22
Ce	113 ± 4	122 ± 5	123 ± 6	120 ± 5
Cs	3.2 ± 0.1	3.7 ± 0.2	3.7 ± 0.2	3.7 ± 0.2
Dy	6.9 ± 0.3	8.5 ± 0.9	8.1 ± 0.3	8.5 ± 0.8
Eu	1.0 ± 0.1	1.2 ± 0.2	1.2 ± 0.2	1.3 ± 0.4
Ga	43 ± 12	116 ± 52	140 ± 23	178 ± 90
Hf	9.7 ± 0.4	10.3 ± 0.3	10.5 ± 0.3	10.3 ± 0.5
La	62 ± 3	68 ± 4	67 ± 11	69 ± 3
Mo	9 ± 2	28 ± 1.4	40 ± 5	50 ± 9
Nd	45 ± 4	47 ± 4	49 ± 7	52 ± 6
Rb	51 ± 3	56 ± 4	57 ± 3	57 ± 8
Sb	2.6 ± 0.1	8.3 ± 0.4	13.0 ± 0.7	20.6 ± 0.7
Sc	12.6 ± 0.5	15.3 ± 0.6	15.8 ± 0.6	16.0 ± 0.2
Se	19 ± 2	59 ± 2	78 ± 2	198 ± 20
Sm	8.2 ± 0.3	9.1 ± 0.4	9.2 ± 0.4	9.7 ± 0.4
Sr	410 ± 60	540 ± 140	590 ± 140	700 ± 210
Ta	2.06 ± 0.09	2.3 ± 0.2	2.5 ± 0.03	2.7 ± 0.1
Tb	0.90 ± 0.05	1.06 ± 0.06	1.10 ± 0.07	1.13 ± 0.06
Th	25.8 ± 0.6	28.3 ± 0.6	29 ± 1	30 ± 2
U	8.8 ± 1.9	16. ± 3	22 ± 4	29 ± 4
V	86 ± 44	178 ± 17	244 ± 18	327 ± 40
W	3.4 ± 0.2	9 ± 2	16 ± 2	24 ± 2
Yb	3.4 ± 0.4	4.1 ± 0.4	4 ± 0.2	4.2 ± 0.3
S (%)	0.101	0.304	0.425	0.711

[a] Weighted average for all determinations, both techniques.
[b] Mass median diameters (mmd) determined by centrifugal sedimentation.
[c] Errors in parentheses are the range for duplicate determinations.
[d] INAA values are the weighted averages of three determinations. Uncertainties are the largest of twice the weighted standard deviation, the range, or our estimate of the accuracy.

INAA – Instrumental Neutron Activation Analysis · AAS – Atomic Absorption Spectroscopy

Table 15: Classification of trace elements based on particle size reported by Coles et al. (1979)

Group I	Al, Ca, Cs, Fe, Hf, K, Mg, Mn, Na, Rb, Sc, Ta, Th, Ti and the rare earths: Ce, Dy, Eu, La, Nd, Sm, Tb and Yb.
Group II	As, Cd, Ga, Mo, Pb, Sb, Se, W and Zn.
Group III	Ba, Be, Co, Cr, Cu, Ni, Sr, U and V.

The groups are defined as follows:

Group I elements show little or no enrichment on the smaller fly-ash particles.

Group II elements increase with decreasing particle size.

Group III elements show behavior intermediate to that of elements in Group I and II.

Their results agree closely with those of Klein et al. (1975). Group II and class II elements are in agreement and show the same behavior. Group II elements are enriched on the smaller particulates and class II are concentrated on the smaller fly ash relative to the larger bottom ash. These data consistencies can be seen in other investigations that are concerned with the concentration-size particle relationship.

Nine well-defined size fractions with mean diameter ranges of 0.5-50 um were measured in fly ash collected from the precipitator of a western coal-fired plant (Campbell et al., 1978). The particles were separated into the nine size fractions using a Bahco Microparticle Classifier, a combination air centrifuge-elutriator. The 43 trace element concentrations as a function

of mean particle size divided the elements into three distinct groupings. These groupings expressed three types of concentrating behavior. Group one elements primarily consisted of the volatile elements or elements partially volatilized during coal combustion and their concentrations decreased with increase particle size. The second group had a minor or direct dependence on particle size and the last group had small changes in their concentration with a maximum concentration at about 5 um. Only a limited number of the elements were presented as belonging to a particular group. But the data in Tables 16 and 17 is partially consistent with the increase in concentration with decrease in particle size of the above trace elements in class II and group II and other concentration-size particle studies.

Similar studies reviewed do not always consistently show the same result when elements are classified according to their concentrations in different size fractions. Measurement of 61 elements in size fractions that was again prepared from fly ash recovered by precipitators at western coal-fired plants (Smith et al., 1980) classified Sb, As, Ba, Br, Cr, Co, Cu, Ga, Pb, Mn, Hg, Nd, Ni ,Se, S, Sn, V and Zn as being significantly enriched in the smaller fraction. But the elements Ba, Cu, Ni, Sb, V and Zn are diversily reported in the literature as having either positive or negative correlation with size (Littlejohn, 1984). Various classifications, when done according to their concentrations in different size fractions, have significant differences in the enrichment of trace elements in size particles. These are attributed to differences in composition of coal, particle size vs efficiency characteristics of the individual electrostatic precipitators, flow rates, and temperature effects on distribution characteristics of the elements (Meserole et al., 1979; Ondov et al., 1979). Evaluating in more detail specific trace element differences in size fractions as reported in the literature is beyond the scope of this paper. It must be noted that differences in trace element concentrations with similar particle size do exist between investigations (Davison et al., 1974; Gladney et al., 1976; Ragaini and Ondov, 1977; Smith et al., 1979; Quann et al., 1982; Weissman et al., 1983; Norton et al., 1986).

In conclusion, trace element increases with smaller particles are the focus of trace element investigations. The increases in group II and class II type elements defined by Coles et al. (1979) and Klein et al. (1975) suggest that very toxic elements of As, Cd, Ga, Mo, Pb, Sb, Se and Zn are being emitted on less than 1 um particulates. This fraction is too small to be collected efficiently by the cascade impactor sampling device, and is usually

deposited inefficiently on back-up filters (Ondov et al., 1979; McElroy et al., 1982). Inefficient sampling of the submicron fraction is a major problem for both concentration - distribution studies and mass balance measurements. To evaluate the direction future research must take to solve these measurement problems, it is essential that there is an assessment of present sampling technology and research.

7. Sampling

Particulates and vapors of the fume are sampled in coal- fired facilities by a variety of sampling techniques. The problems in obtaining reliable measurements of size and concentration of the particulates are considerable when reviewing past performance of the sampling equipment. Especially problematic is obtaining reliable measurements of the size and concentration of the submicron particles that are entained in the gas and aerosols of the fume. This section will define present sampling technology for the different size particulates, aerosols, and gases, with emphasis on the specific problems encountered in sampling techniques.

7.1 Sampling apparatus

Most fly ash is in the 1 - 20 um range and a small amount which is approximately 1% by mass, is in the submicrometer range (Amdur et al., 1986). The larger particulates are sampled on line by cascade impactors or staged cyclones with back-up filters for collection of submicron particulates. Anderson high volume cascade impactor, Lovelace multiple jet cascade impactor, Mark 10 impactor and Meterorology Research, Inc. cascade impactor are a few of the commercially available impactors. Cascade impactors have a series of plates called impactor stages (Figure 3) that collect successively smaller particles. The particulates enter directly into cascade impactors for on-line aerodynamic size classification. Two reported aerodynamic diameter ranges of impactors are 0.2 - 50 um (Ondov et al., 1978) and 0.3 - 15 um (Sem, 1984). Classification gives information on size distribution of particles in the the fly ash as well as limited particle concentration resolution. Impactor plate collection surfaces are made of polyethylene or polycarbonate materials or are a stainless steel disk (Gussman et al., 1973; Meij et al., 1984; Markowski, 1984; Markowski and Filby, 1985; Y.-S. Cheng et al., 1985).

It is known that in sampling the performance of the cascade impactor is

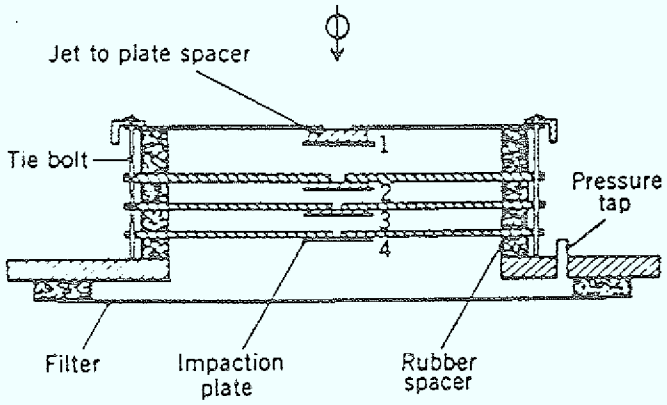

Figure 3: Schematic cutaway view of high volume cascade impactor.(After Gussman et al., 1973)

limited by problems associated with wall loss, particle bounce from a larger stage to a smaller size stage and reentainment of collected particles (Dzubay et al., 1976; Gladney et al., 1976; Campbell, et al., 1978). Wall loss is from interstage losses of particles onto the channels which carry the flow from one stage to another. This results in the reduction of the measured concentration of smaller particles (Sem, 1984). Interstage losses can be severe enough that the emission factors of elements that are derived from these filter samples vary greatly between successively collected samples, thus accurate comparisons of values can not always be made (Ondov et al., 1979). Wall loss effects are believed to be the most serious error, since they can range from 30-50 % of total amount collected (Valkovic, 1983). Bounce of large particles from a larger stage where they belong to a smaller size stage, can include loss to the final back-up filter for the submicron fraction. This greatly distorts size distributions by making it appear as if there are a greater number of smaller particles. This has a tendency to limit the upper particle size collection to 10 - 20 um. Reentainment, sometimes referred to as blowoff of particles, is the blowoff of previously deposited particles on impaction stages that results in redepositing of particles on smaller size stages or complete loss of particles (Sem, 1984).

Reentainment and particle bounce of cascade impactors are minimized by the use of greased substrates on the impaction plates (Apiezon L and H greases) or peelable Kapton films that are attached to the stainless steel collection disks and coated with Apiezon L grease. (Quann et al., 1982; Meij et al., 1984; Y.-S. Cheng et al., 1985; Markowski and Filby, 1985). Glass fiber filter material, clamped onto the steel disks, can be used when grease

becomes unstable at high flue gas temperatures (McElroy et al., 1982). Quann et al. (1982) constructed "a conical head with a porous carbon inner wall through which gas was transpired at a nominal rate" to minimize deposition on the entrance wall of the impactor. Impactors are now being ran at lower sample flow rates (and near in situ pressure) to reduce the effects of particle blowoff and reentrainment (Markowski and Filby, 1985). A very recent study has determined that lower jet velocities shorten sampling times and a duplicate sixth stage inserted between the usual sixth and final seventh stage of the impactor reduces blowoff. Under the conditions of the study, it was reported that the jet velocity had the most influence on blowoff and that other variables were not as important. Grease thickness on the impactor collection disk was found to have less of an influence because the low-blowoff stages were maintained dry, while the high-blowoff stages were greased soaked. Total gas volume sampled and stage loadings were also determined not to be important. The study highly suggested that examining impactor size distribution data for a correlation with jet velocity is a useful method to check for blowoff (Markowski, 1984).

A cascade or staged cyclone collects particles from the stream by whirling it around a cylindrical chamber. By whirling it faster in a cyclone with a smaller diameter, particles with smaller aerodynamic diameter can be collected. The diameter at which 50% of the particles are removed from the stream is called the aerodynamic cutoff diameter. As with the impactor, successively smaller cutoff diameters are connected in a series, and the combined assembly is known as a cascade cyclone. Cascade cyclones collect larger deposits than impactors, up to several grams per stage, without blowoff or bounce difficulties. They are therefore preferred for high concentration aerosols, while impactors are preferred for low concentration aerosols (Sem,1986). Impactors are reported to be more efficient at separating ash into fractions than the staged cyclones (Y.-S. Cheng et al., 1985) and it has been reported in the study by Meserole et al. (1979) that when two sampling devices were used only the results of the impactor were discussed because of its greater efficiency in fractionating the particles. In comparison with the cascade impactor, the cascade or staged cyclone is less frequently used in the reviewed sampling studies. It was found to be combined in parallel with the cascade impactor when in- plant sampling was performed (Meserole et al., 1979; Y.-S Cheng et al., 1985).

Final back-up membrane filters are used for the submicron fraction collection and to minimize losses of the cascade impactor. Backup filter materials can consist of borosilicate glass-fiber, plastics, or quartz

(Meserole et al., 1979; Ondov et al., 1979; Markowski, 1984). The 47 mm diameter, 0.4 um pore Nuclepore back-up filter is frequently mentioned in the literature as the filter used. If a small fraction of the larger particulates are bounced off and collected on the back-up filters during sampling, then large errors in measured amounts of the submicron fraction will result. This problem is severe in the flue gas for particles of less than 1 um diameter because concentrations above this size are substantially greater (Markowski, 1984).

Cascade impactors or staged cyclones and back-up filters are part of the assembage of equipment called a sampling train that is combined to sample the various fractions of the coal-fired power plant stream. Since sampling is performed under a wide variety of conditions, no single sampling train can be used in all circumstances and therefore are varied in specifications. A very comprehensive train is the U.S. Environmental Protection Agency's sourse assessment sampling system (Figure 4). It consists of a nozzle joined through a probe to a three series cyclone, a filter, and a final series of impingers or gas scrubbers. Since some trace elements in a coal-fired plant are found mostly in the volatile-phase, there must be an adequet collection of the gases to recover trace element vapors. The collection of the vapor phase is usually by the impinger train down stream of the impactor. The impingers are of pyrex glass and contain solutions for the collection of specific gases.

There are sampling problems associated with the collection of gases in impinger trains. Solution reagents used in sampling of gases can gain from their container trace element concentrations or lose them by adsorption on to it and both can cause serious errors. Since interference can not be entirely eliminated it has to be minimized by using pyrex or polyethene materials that are leached before use, and all vessels in which reagents are used or stored need to be preconditioned. In addition, strongly recommended are the minimizing of storage times and the inclusion of blanks with all samples analyzed (Littlejohn, 1984).

Very recently there has been reported by Fogg (1986) a volatization artifact in sampling that may be an additional problem in sampling of vapors. It is proposed that the gaseous uptake by the untreated collection media itself, could affect trace element measurement in the gases of a cold-fired plant. This could be potientially important for the elements Cl, Br, Hg, S and B that are in the gas phase. It was stated that there is no data that presently relates the uptake of gaseous componets to a specific impaction

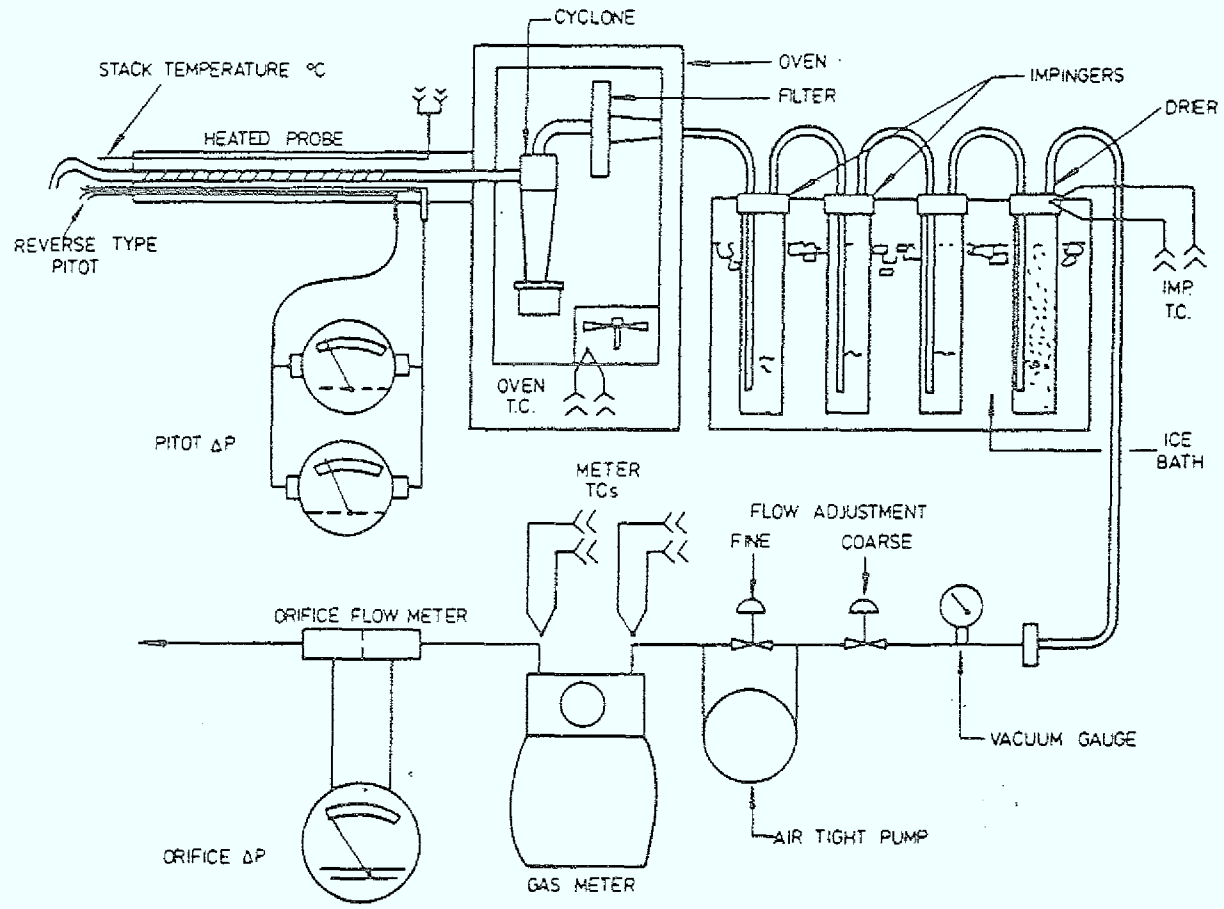

Figure 4: EPA source assessment sampling system. (After Littlejohn, 1984)

surface but there are preliminary results on the uptake of gaseous B(OH)3 and HCl by uncoated Whatman 41 filter paper (cellulose fiber) in a Battelle-type cascade impactor in laboratory conditions. The amount of absorption was indicated to be in part directly proportional to contact time of the gas stream with the impaction surface. The researcher pointed out that even small amounts of gas uptake could strongly influence measured size distribution of certain elements. It was concluded that there must be careful attention "paid to the selection of the appropriate filter medium for use in cascade impaction."

In sampling, if the mass of particles captured and the total volume of the gas stream passing through the sampling device are measured accurately then the particulate concentration in the gas stream can be obtained. For a sample to be representative of size distribution and concentration of the

particles in a gas stream, isokinetic sampling is required. Isokinetic sampling is when the velocity of the gas drawn into the nozzle is maintained equal to the velocity of the gas approaching the nozzle (Muir and Akinola, 1986). Isokinetic collected samples should represent correct concentration, mass, and distribution of the solids but the low particulate loadings make it difficult to collect sufficient material for these determinations (Meserole et al., 1979; Littlejohn, 1984; Meij et al., 1984; Y.-S. Cheng et al., 1985). In addition nonuniform loading of the particles on sampling filters results in biased data because the location of the ash sample taken off the filter for chemical analysis may not be a true representation of composition and size distributions (Norton, 1986). These difficulties have forced some studies to use ESP ash as representing the fume. The problem with this type of representation is that the bulk composition of emitted fly ash is quite different from ESP ash (Meij et al., 1984; Markowski and Filby, 1985).

In the past, maintaining correct isokinetic sampling conditions was done by selecting the appropriate nozzle orifice diameter for the sampling probe system, based on the gas velocity, stack temperature, and stack pressure (Norton et al., 1986; Muir and Akinola, 1986). The control valve is usually adjusted manually until isokinetic conditions are obtained. In the high temeprature conditions of a coal-fired plant, the gas temperature and/or flowrate do not remain constant but can vary considerably during operation. In manually setting isokinetic conditions, the valve adjustment can "lag considerably behind the actual changes in conditions, causing significant errors in sampling (Muir and Akinola, 1986)." Therefore, isokinetic conditions are usually approximated.

A new method of automating a gas stream sampling train is being developed by Muir and Akinola (1986) "in order to reduce significantly the errors in sampling." The sampling of dust-laden gases in a duct or chimney is performed by automating the gas stream sampling train with a microcomputer. The gas sampling apparatus is automated by interfacing the appropriate parts of the sampling train with a microcomputer. "A assembly Language program, which can be used with any sampling train arrangement, has been developed to compute the correct sampling conditions. The microprocessor then transmits the appropriate signal to a control valve for regulation of the sampling rate." Hence, isokinetic conditions are maintained. The instrument is still in the development stage. A portable instrument and prevention of the plugging of the pitot tube are their future research objectives.

The obtaining of reliable measurements of size distribution of the

submicron particles in coal-fired plants utilizes different sampling instruments other than the conventional sampling train. A TSI model 3030 electical aerosol analyzer (EAA) is frequently used in combination with impactors to cover the size distribution measurement of the submicron aerosols, giving a more detailed distribution in the submicron size range (Mc Elroy et al., 1982; Y.-S. Cheng et al., 1985; Markowski and Filby, 1985). The EAA is frequently used to measure size distributions of particles below 0.5 um in diameter. The non-aerodynamic technique does not measure aerodynamic size directly like the impactor, but particle sizes where aerodynamic diameter is not important (Sem, 1986). EAA classifies aerosols between .001-1.0 um, as reported by Markowski et al. (1980), and in combination with impactors can cover a reported broader range of 0.005 -10 um (Y. -S. Cheng et al., 1985). The combination of the impactor and EAA data was used to demonstrate the collection of considerable blow-off and particle bounce of the impactor. This was reflected by the large disagreement in size distribution data overlap in Figure 5 (Markowski, 1984). The EAA and impactor used in combination does afford a wide range of size distribution, but for the number and mass distribution of the combined data there must be a conversion by calculation to equality of the volume and mass of the particles (Y.-S. Cheng et al., 1985).

Another method recently developed for size separation of fly ash, is the continuous steric field-flow fractionation. This is an optical particle size monitor that is being developed by the U.S. Environmental Protection Agency for measurement of particle size for in-stack source testing. The results indicated that when compared to a cascade impactor, the measurements defined similar particle size distributions between 0.2 and 20 um and particles smaller than 0.2 um are not observed by the optical sizer. Particles larger than 20 um are also not expected to be detected, but it was stated that the optical instrument may have some sensitivity to the larger size particles (Conner and Knapp, 1985).

The TSI differential mobility particle sizer is also used for size and concentration resolution where aerodynamic diameter is not important. The submicron particles are classified into size ranges between 0.01-0.8 um diameter (Sem, 1986). This instrument was not referred to in the in-plant sampling studies but as part of an experimental coal combustion sampling system (Amdur et al., 1986).

A new approach for the determination of the size and concentration of particles entrained in a gas has been proposed in a paper by Tate et al. (1986).

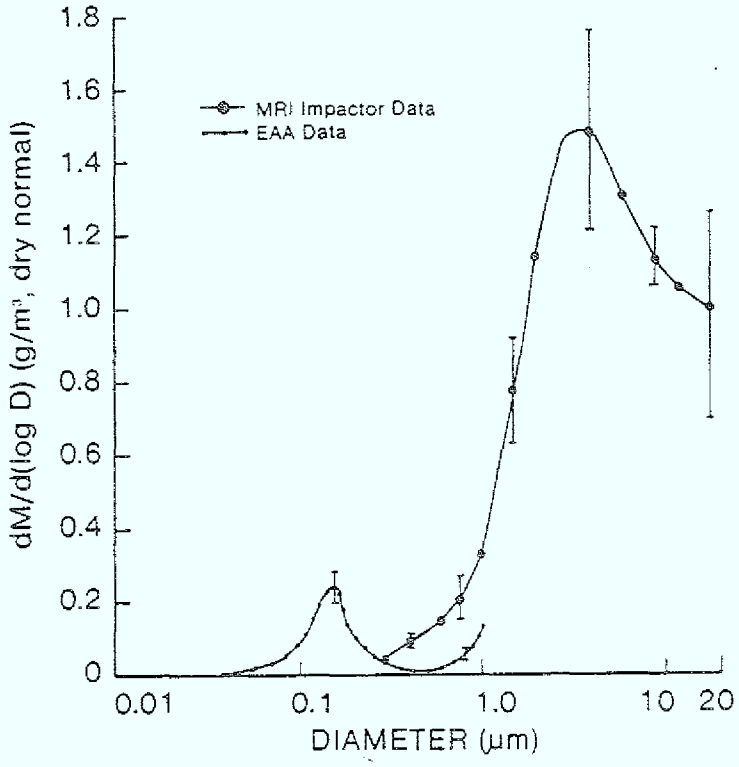

Figure 5: Typical size distribution measured by EAA and cascade impactors. Error bars on the cascade impactor data show the standard deviation of four runs with constant boiler load. Error bars on EAA data show typical variation over a 1-hr sampling period. (After Markowski, 1984)

The development of an on-line sampling instrument was discussed for the direct measurement of the aerodynamic diameter of particles in situ without sampling to avoid the unreliability of previously mentioned techniques. In principle, it is proposed that " a pitot-static probe can be inserted into the gas flow, with a fibre-optic laser-Doppler system that measures particle velocities. The particle size distribution can be built up by measuring the velocity and calculating the size of each particle detected during a brief time interval, while the number of particles detected can indicate the particle concentration. Since there would be no need to sample the gas flow and because the optical and electronic components can be isolated from the gas flow, this technique should be particularly suitable for gases at high temperatures."

The problems in obtaining reliable measurements of the size and concentration of particles from the sampling of coal-fired combustion

products have not been solved sufficiently. Although new improvements are being made in sampling technology, there is still a need for more laboratory development and improvement of sampling apparatus that will afford better in-plant collecting, especially of minute particles and gases. Present laboratory experimental coal combustion studies that show improvement in mass balance measurement are done in ideal conditions that include closed systems. These laboratory conditions can not be compared entirely to in-plant sampling. They do give a strong indication that in-plant sampling can be greatly improved. In the final analysis, to perform accurate and precise sampling of coal-fired combustion particulates and vapors, one sampling approach or apparatus is not the answer. A combination of improved accurate on-line equipment that does very specific size and phase collection should be used to increase the accuracy of trace element determination in coal-fired facilities. It must be stressed that research is not only needed in sampling technology but a more universal sampling system of coal-fired facilities should be introduced. This can only increase efficiency in sampling and allow for more accurate comparisons between similar coal-fired plants.

8. Analytical Technique

Preference for a particular analytical technique is often expressed in the literature and these preferences are usually the result of availability of equipment and the individual's experience. More recently the trend in analytical technique has been toward multielemental instrumental procedures to quantitatively cover as many elements as are applicable. In general, coventional chemical analytical techniques are not done due to the lack of sensitivity needed to measure trace quantities. Therefore, the primary methods used for trace element analysis of coal combustion products were found to be instrumental nuclear activation analysis, X-ray fluorescence, spark sourse mass spectrometry, atomic emission spectroscopy, atomic absorption, optical emission spectroscopy, and inductive coupled argon plasma emission spectroscopy. The use of any analytical technique needs accuracy limits and consistency. But even though an analysis is accurately performed, it may or may not be correct because of the fundamental problems in sampling. At the same time, there are still some basic guidelines and problems that need to be addressed because analytical technique inaccuracy does cause systematic errors in mass balance determinations.

The use of appropriate standards and sample preparation for analysis of coal and coal ashes should not be underestimated. In a program initiated by the U.S. Environmental Protection Agency (EPA), results which were published by Von Lehman et al., (1974), portions of the same coal and fly ash samples were sent to nine laboratores to determine up to 28 elements by six analytical methods. The results from the various methods and laboratories for most elements showed enormous variations far outside the uncertainty limit quoted for the technique used. For this reason it was clear that standards were badly needed so laboratories could check their procedures. The results of another interlaboratory comparison study by the EPA on coal and fly ash standard reference material obtained satisfactory agreement on the measurement of 30 elements using instrumental nuclear activation methods. This study showed that with great care in measurement technique it is possible to obtain satisfactory agreement between laboratories and that there is a need for standards in the calibration of instruments (Ondov et. al., 1975). The current standards most used for trace element analyses of fly ash and coal are the National Bureau of Standards Reference Material (NBSRM) 1633 and NBSRM 1632 (Quann et al., 1982; Weissman et al., 1983; Conzemius el al., 1984; Norton et al., 1986).

Sample preparation offers opportunity for sample contamination through wet or dry ashing of coal or the dissolution of fly ash through acid treatment or fusion. It is specific to the method of analysis used. In atomic absorption spectroscopy (AAS) sample dissolution is required and no single technique is equally satisfactory for dissolution of all samples. A coal sample requires dissolution techniques capable of decomposing large quantities of organic material. Slag and fly ash require techniques capable of dissolving acid-resistant minerals and glasses. Very often some kind of ashing of the sample is performed and volatilization losses of certain elements occur during ashing procedures and pretreatment. This can be a limiting factor on what type of sample an analytical procedure like AAS may be applied. Analysis by atomic absorption or optical emission usually requires an ashed sample. Sometimes the need for extensive pretreatment of coal samples produces ash element data that cannot be related back to the whole coal. In contrast, instrumental neutron activation analysis and X-ray emission spectroscopy can be applied to any matrix and require no sample pretreatment. (Valkovic, 1983; Littlejohn, 1984).

Even though it is felt that detection limits with instrumental analysis can be good with use of appropriate standards and sample preparation,

precision still depends largely on individual analytical skill. Despite new instrumental high sensitivity in determination of small quantities of elements, at the present time neither the reproducibility of measurements of trace elements by one technique nor the agreement between different techniques reaches the standards expected in conventional analysis. The situation exists because of a combination of factors, which includes in-plant sampling, contamination of the sample during preparation and inadequate standardization of equipment. Ideally, any method of analyzing trace elements in coal combustion products should determine a large number of elements of interest simultaneously, be reproducible and have relatively little sample preparation. None of the available techniques determine all the elements and none can be considered absolutely accurate. The approach that is presently regarded as the most effective combines two analytical techniques and uses the comparison to indicate agreement (Clevenger et al., 1984; Littlejohn, 1984). Ultimately, there is a definite need to resolve the ambiguities of trace element analytical measurement in coal and fly ash through standardization, analytical skill, and better sampling.

9. Conclusion

In this literature review, the evaluation of the seven principle coal-fired plant mass balance investigations verified that certain prevailing problems are existent in trace element mass balance determinations. The large positive and negative imbalances for many elements (As, B, Br, Cl, Co, Cr, F, Hg, Se, Sb and Zn) indicate the inability to determine accurate concentrations in the different phases. These elements are known to be volatile at combustion temperatures and are thought to condense out on surfaces of either larger residual ash particles or submicron particulates, while others remain in the gas phase. Most trace element studies have looked at enrichment in ash fractions or size particulates relative to mass balance determinations. The use of enrichment factors calculated from concentrations in these fractions do reflect partitioning behavior in ash and vapor but not specific concentration levels. Present emission values that are derived from mass balances are doubtful and still need substantiation from more precise measurements. The fundamental problem in mass balance and enrichment determinations is accurate in-plant sampling of the ash and gases. Present sampling of the submicron particulates, aerosol, and gases is difficult and available techniques are inadequate. Improvement in sampling technology is regarded as priority in the improvement of mass balance

measurements. Analytical technique is a minor consideration. In the long-term, improved mass balance determinations will bring about greater accuracy in estimating emission values. In addition, it will afford the establishment of a data base from which a comparison can be made between trace element concentrations in similar and different coal plant technologies. And most signficantly, this will secure an understanding of how to handle any environmental toxicity or hazard that may be present.

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