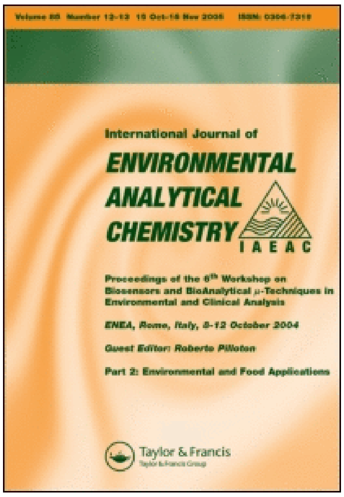

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Metal Content of Stack Emissions, Coal and Fly Ash from Some Eastern and Western Power Plants in the U.S.A. as Obtained By ICP-AES

Shane S. Que Hee[a]; Vincent N. Finelli[a]; Fred L. Fricke[b]; Karen A. Wolnik[b]
[a] Institute of Environmental Health, University of Cincinnati, Cincinnati, OH [b] U.S. Food and Drug Administration, Cincinnati, OH

To cite this Article Hee, Shane S. Que , Finelli, Vincent N. , Fricke, Fred L. and Wolnik, Karen A.(1982) 'Metal Content of Stack Emissions, Coal and Fly Ash from Some Eastern and Western Power Plants in the U.S.A. as Obtained By ICP-AES', International Journal of Environmental Analytical Chemistry, 13: 1, 1 — 18

To link to this Article: DOI: 10.1080/03067318208071579

URL: http://dx.doi.org/10.1080/03067318208071579

Intern. J. Environ. Anal. Chem., 1982, Vol. 13, pp. 1–18
0306-7319/82/1301-0001 $06.50/0

Printed in Great Britain

Metal Content of Stack Emissions, Coal and Fly Ash from Some Eastern and Western Power Plants in the U.S.A. as Obtained By ICP-AES

SHANE S. QUE HEE† and VINCENT N. FINELLI
Institute of Environmental Health, University of Cincinnati, Cincinnati, OH 45267

FRED L. FRICKE and KAREN A. WOLNIK
U.S. Food and Drug Administration, 1141 Central Parkway, Cincinnati, OH 45202

(*Received October 20, 1981; in final form, March 1982*).

The metal profiles characterizing stack emissions, fly ashes and coals of three coal-fired power plants in the United States using one high-sulfur Eastern and two low-sulfur Western coals were obtained by quantitating 21 elements via inductively coupled plasma atomic emission spectroscopy. The stack emissions were collected with a modified sampling train approved by the U.S. EPA. Aluminum, calcium, iron, sodium, potassium and magnesium predominated in all the samples and the emission was greatest from the high sulfur coal. Silicon could not be accurately quantitated because of the digestion procedure used. Volatile elements were lead, zinc, beryllium and molybdenum. Chemical speciation in stack emissions was shown to be important by atypical collection for Pb, Bi, Be, Na, Cu and Zn in the three impingers of the sampling train.

KEY WORDS: Inductively coupled plasma atomic emission spectroscopy, metals, stack emissions, fly ash, coal.

INTRODUCTION

The major pollution control devices present in the stacks of most coal-fired power plants are electrostatic precipitators which are from 95 to 99.5 percent efficient in total mass collection. The respirable particles ($<5\,\mu$m in aerodynamic diameter) largely escape and constitute the bulk of the stack emissions.[1] These particles have high probability for pulmonary deposition,[2] and any adsorbed toxicant can also be transported into the alveoli to be solubilized eventually and hence rendered available to exert its adverse effects. Since coal use for electric power generation is expected[3,4] to reach 7.7 × 10^{11} kg in the U.S.A. by 1985, release of stack emissions into the atmosphere is likely to increase, along with any associated inhalation hazard. For example, dimethyl sulfate, a known animal carcinogen, has been detected in coal fly ash and on airborne particulate matter.[5]

Although many studies have been published on the chemical compositions[6-16] and toxicity[6,17-21] of various fly ashes, comparatively few publications have appeared concerning the elemental composition of the stack emissions. Andren *et al.*,[22] Zoller *et al.*,[23] Ondov[24,25] and the U.S. EPA[26] have published data on this topic. Andren *et al.* investigated the emissions of three Southern power stations; Zoller *et al.* evaluated those from two 355 MW Units of an eastern coal-burning power plant; Ondov[24,25] reported on the results of tests on two western power plants burning low sulfur subbituminous and bituminous coal, and noted that the emissions were rich in S, Fe, Al, Ca, Mg, F and Ti. The U.S. EPA[26] has also published data on emissions from three Midwestern power plants utilizing sub-bituminous and lignite coal. Deposition of these emissions at ground level depends on many variables, e.g., particle size, wind speed and direction, atmospheric moisture and land topography. Klein and Russell[27] found that soils around a coal-burning power plant were enriched in Ag, Cd, Co, Cr, Cu, Fe, Hg, Ni, Ti and Zn, but other investigators have found no significant enrichment in soils around power plants.[7,28] Klein and Russell[27] also reported that vegetation in the fall-out zone around a power plant were enriched in Cd, Fe, Ni and Zn.

Although there may be controversy over the health and ecological effects of stack emissions there is no doubt that more data, both chemical and toxicological, are required to assess the impact of stack emissions on the biosphere. We have therefore collected stack emission condensates from three power plants burning coals originating from the Eastern and Western United States. In this first paper, the trace metal fingerprint of the stack emissions, fly ashes and original coals will be presented. Other papers in the series will report on the toxicological properties of the condensates, and the compounds responsible for the observed toxicity.

EXPERIMENTAL

Sampling of stack emissions

Power Plants and Coal Types: Sampling of stack emission condensates was performed at three different coal-fired power plants in October, 1977.

One of the power plants was the Cincinnati Gas and Electric Company's Walter C. Beckjord station in New Richmond, Ohio. This station utilizes Eastern bituminous coal from the Collins Mining Company in Lawrence County, Ohio. The second power plant investigated was the Pacific Power and Light Company's Jim Bridger Station near Point of Rocks, Wyoming. Western sub-bituminous coal from the nearby Jim Bridger Coal Mine in Sweetwater County, Wyoming is utilized. The third station was the Dave Johnston Station in Glenrock, Wyoming, which burns Western sub-bituminous coal from the adjacent Dave Johnston Mine in Converse County, Wyoming. Two samples were taken on consecutive days for the latter plant. Power plant, coal, unit and stack characteristics of the stacks sampled are presented in Table I.

TABLE I

Power plant characteristics

Location	Bridger Point of rocks, Wyoming	Johnston 1a Glenrock, Wyoming	Johnston 1b Glenrock, Wyoming	Beckjord New Richmond, Ohio
Coal parameters				
Air dry loss %	1.4	0.30	3.3	5.3
Moisture %	17.4	10.5	18.5	3.65
Ash %	6.51	9.64	9.21	20.6
Sulfur	0.41	0.52	0.47	2.8
Volatile matter %	29.3	37.1	36.0	31.0
Heating value (BTU/lb)	10,300	9,780	8,850	10,800
Coal used in 1976 (tons)	1,900,000	2,800,000	2,800,000	2,637,890
Stack parameters				
Power of unit sampled (MW)	475	110	110	125
Number of pulverizers	6	5	5	4
Maker of stack electrostatic precipitator	General Electric	Lodge Cottrell	Lodge Cottrell	Research–Cottrell
Stack area (m^2)	109	8.75	8.75	14.8
Sampling parameters				
Barometric pressure (cm Hg)	62.8	63.2	63.2	74.8
Stack gas temp. (°C)	132	140	140	166
Stack gas velocity (m/s)	9.66	24.7	24.9	18.6
Stack gas flow: actual (m^3/min)	63,400	13,000	13,000	16,500
Standardized flow (m^3/min)	37,800	7,770	7,710	10,800

Sampling Train: A modified U.S. EPA Method 5 sampling train[45] was used. This consisted of a heated, pyrex-lined probe equipped with a stainless steel 316 nozzle of critical orifice ~1 mm together with three Greenburg–Smith pyrex impingers interconnected by pyrex ball-and-socket joints, (the impingers were modified by replacing the tips with a 1.27 cm ID pyrex tube extending to 1.27 cm of the impinger flask bottoms); at the exit end of the third impinger was a filter-holder containing a 3″ diameter Gelman type-A glass fibre filter held at 121°C followed by a fourth modified Greenburg–Smith impinger containing 500 g of activated silica gel maintained at 20°C and a metering system consisting of a vacuum gauge, leak-free fibervane pump (Gast), thermometers and a dry-gas meter (Rockwell) to maintain an isokinetic sampling rate and to determine sample volumes. The first two impingers each contained 100 mL of water and the third was initially dry.

The first three impingers therefore collected both particulates and vapor. In the official U.S. EPA method,[45] the position of the filter is before the first impinger, thus allowing only vapor phase species to be trapped. The whole system was checked for leaks before sampling and when any sampling train components had to be changed. Leakage rates were always less than 9 mL/sec. All stacks were sampled at the same distance after the electrostatic precipitators at all three plants using four probes, each probe being backed by its sampling train. All impingers were cooled by being immersed in a solution of crushed ice.

Stack operation characteristics: All gas velocities in the stacks were measured with a calibrated S-pitot tube and an inclined draft gauge (Dwyer). Velocities were measured at each sampling point across the stack diameter to determine an average value according to the method 2 procedure of the Federal Register.[45] Temperatures were measured with a precalibrated thermocouple.

Several grab samples of the stack gases were collected in the manner described in Method 3 of the U.S. EPA official method.[45] This gas sample was then analyzed for carbon dioxide and oxygen content using Fryrite gas analyzers, similar to Orsat apparatuses.

Sampling conditions and subsequent storage: Sampling conditions of the stacks are presented in Table I, and the sampling parameters of the impinger train are given in Table II for all plants. Isokinetic sampling rates were set with a nomograph as suggested in the Federal Register reference above. Velocity traverses with the pitot tube were made on the entire duct at the level of the four sampling probes to determine the velocity profile of the gases. After sampling at each location, all fluids in the corresponding impingers were amalgamated to form solutions of

TABLE II

Sampling parameters of the collection trains

A. JIM BRIDGER PLANT	Train 1	Train 2	Train 3	Train 4
Nozzle size (mm)	9.65	9.65	9.65	9.65
Impinger temp. (°C)	8.33	8.33	7.78	7.78
Volume of water	1.89	1.75	1.99	2.05
Volume of water collected (L)				
Meter volume (m^3)	40.7	41.9	43.5	43.7
Meter temp. (°C)	15.2	28.8	29.2	16.9
Average pump pressure (cm Hg)	20.3	20.3	40.6	22.9
Sampling time (min)	1409	1402	1386	1380
Volume sampled standardized (m^3)	34.4	33.9	35.2	36.8
B. DAVE JOHNSTON 1a				
Nozzle size (mm)	6.35	6.35	6.35	6.35
Impinger temp. (°C)	18.9	18.9	18.9	18.9
Volume of H_2O collected (L)	2.58	2.43	2.56	2.49
Meter volume (m^3)	47.2	46.9	44.8	40.2
Meter temp. (°C)	32.5	48.9	48.6	28.2
Average pump pressure (cm Hg)	22.9	22.9	22.9	22.9
Sampling time (min)	1440	1440	1440	1440
Volume sampled standardized (m^3)	37.9	35.7	34.3	33.3
C. DAVE JOHNSTON 1b				
Nozzle size (mm)	6.35	6.35	6.35	6.35
Impinger temp. (°C)	15.0	13.3	12.8	16.1
Volume of H_2O collected (L)	2.31	2.60	2.48	2.48
Meter volume (m^3)	50.9	47.6	45.3	41.8
Meter temp. (°C)	33.7	48.6	45.3	26.7
Average pump pressure (cm Hg)	33.0	36.8	20.3	7.62
Sampling time	1440	1440	1440	1440
Volume sampled standardized (m^3)	41.0	36.6	35.0	34.2
D. WALTER C. BECKJORD				
Nozzle site (mm)	6.35	6.35	6.35	6.35
Impinger temp. (°C)	22.8	16.7	20.0	15.6
Volume of H_2O collected (L)	0.940	1.23	0.875	0.730
Meter volume (m^3)	30.7	33.0	24.9	18.1
Meter temp. (°C)	31.4	31.1	24.2	26.4
Average pump pressure (cm Hg)	7.62	7.62	10.2	12.7
Sampling time	1320	1202	1200	1200
Volume sampled standardized (m^3)	29.3	31.5	24.2	17.5

known volume corresponding to impingers 1, 2 and 3. Thus sampling of stack emissions of each power plant produced three distinct samples for analysis; impinger 1, impinger 2 and impinger 3. All were stored individually in labeled and sealed pyrex bottles at 4°C until required for analysis.

Processing of samples: The impinger amalgamates were acidic (pH ~2.0). Those containing heavy particulate matter were of higher pH. Prior to taking 5 mL samples for analysis, the amalgamates were equilibrated at room temperature and then sonicated for six 20 second intervals to resuspend the particles. All samples of coal and fly fish ash were ground to a fine dust to provide representative 50 mg samples for analysis. All samples were allowed to react with 10 mL 3:2 concentrated nitric/perchloric acids contained in metal-free teflon beakers, previously soaked overnight in 50% nitric acid. A metal-free watch glass was placed over the beaker and solutions were allowed to incubate at room temperature overnight (16 hours). The contents of the beakers were then refluxed at 90°C until the solutions became colorless. The watch glasses were finally removed to allow evaporation of the nitric acid. The temperature was then raised to ca. 150°C and the perchloric acid just evaporated. The residue was reacted with concentrated hydrofluoric (HF) acid (15 mL) at 120°C until no turbidity was evident; 2:1 concentrated HF/HNO_3 (15 mL) was then added, heated at 120°C for 2 hours, 1 hour at 150°C and just evaporated at 120°C. The residue was taken up in a known volume of warm 8% (W/W) HNO_3 and the solution transferred quantitatively via a metal-free Pasteur pipette to a calibrated ground glass graduated cylinder. All volumes were adjusted to 10 mL with 8% HNO_3 acid. This technique is similar to one used by Hartstein *et al.*[29] to obtain quantitative (>93%) recoveries of Be, Cd, Ca, Co, Cu, Li, Mg, Mn, Ni and K. Some Si and perhaps B will be partially lost because of the evolution of the volatile fluorides during the hydrofluoric acid digestion step.

Multi-element analysis: The samples were subjected to multi-element analysis by Inductively Coupled Argon Plasma-Atomic Emission Spectroscopy (ICP-AES) with a Model 1160 instrument (Plasma Atom Comp., Jarrell–Ash Division, Fisher Scientific Company, Waltham, Massachusetts).

The nebulizer was of the non-adjustable cross-flow type (Part No. 003444; Jarrell–Ash Division) operated under the following conditions: plasma torch (Quartz type, 1 mm nozzle diameter); argon gas flows (Coolant–18 L/min; Sample–0.35 L/min at 35 PSI); solution uptake by the Gilson Minipuls II peristaltic pump (1.28 mL/min); forward RF power

(1 kW); reflected RF power (<5W) and an induction coil comprised of a three-run water-cooled copper tubing.

The optics were set as follows: focussing element (separate off-axis front-surfaced concave mirrors); magnification (×3.6); height of observation of spectra (15 mm above the coil) and entrance slit aperture (3 mm). Direct reader components were defined to be: entrance slit (25 μm); exit slits (50 μm); grating (2400 gr/mm ruled concave); blaze (300 nm) and dispersion (0.53 nm/mm first order). Atomic emissions were recorded by Hamamatsu type R427 (160–320 nm), R300 (250–650 nm), R300 B (Na) and R889 (K) photomultipliers operated at the recommended voltages. Read-out was effected by a Central Processing Unit (PDP 11/34, DEC, Maynard, Mass.) controlled individual op-amp analog with multiplexed A/D converters. Line and Background integration periods were set at 20 and 10 seconds respectively. Visualization was by a CPU terminal (LA-36 DEC writer—DEC, Maynard, Mass.). CPU mass storage was accomplished by RL 01 Fixed Head Discs (DEC, Maynard, Mass.).

The analytical wavelengths (in nm) chosen for element analyses were: Al (308.2), B (249.7), Ba (493.4), Be (313.0), Ca (396.8), Co (228.6), Cr (267.7), Cu (324.7), Fe (259.9), K (766.5), Mg (279.5), Mn (257.6), Mo (202.0), Na (589.0), Ni (231.6), P (214.9), Pb (220.3), Si (288.1), Sr (421.5), Ti (334.9) and Zn (213.8). Metal standards were analyzed using 8% nitric acid. Background corrections were also applied for Ba, Be, Co, Cr, Cu, Mn, Mo, Ni, P, Pb, Si, Ti and Zn. Detection limits in ppb were: Al (20), B (2), Ba (1), Be (2), Ca (2), Co (2), Cr (10), Cu (2), Fe (6), K (20), Mg (2), Mn (1), Mo (5), Na (2), Ni (5), P (40), Pb (10), Si (10), Sr (1), Ti (2) and Zn (3).

The elemental content was calculated for each impinger, and the total for each stack found by addition. The trace metal concentration in each stack emission was then found by dividing the total metal content by the standardized volume sampled. All elemental contents in fly ash and coals were expressed in μg element/g of original sample. The concentrations of selected metals (Al, Be, Cr, Cu, Fe, Mn, Ni, Pb, Zn) were also verified by atomic absorption spectroscopy using the appropriate conditions and analytical wavelengths,[30] after the digestions were repeated again in fresh starting material.

RESULTS

Metal levels for the nine elements determined by both ICP-AES and AA method agreed within ten percent. The levels for Cd, Ca, Co, Li, Mg and K are also expected to be accurate,[29] as are the levels for such other metal species as Ba, Na, Sr, Ti and Mo.[47] B and Si values will be low because of the evolution of volatile fluorides,[47] unless B is already in the borate form,

TABLE III

Approximate order of relative abundance of individual elements in corresponding coals (A), fly ashes (B), and recovered stack emissions (C)

		Relative abundances (%) in											
		Western 1a			Western 1b			Western 2			Eastern 1		
Element	DL (ppb)	A	B	C	A	B	C	A	B	C	A	B	C
Al	20	28300^a	103000^a	344^b	21300^a	141000^a	733^b	9720^a	103000^a	1130^b	50200^a	83500^a	23300^b
Al	20	100	100	100	100	100	100	100	100	100	100	100	100
Ca	2	86	46	66	124	43	67	65	44	63	6.5	11	7.2
Fe	6	21	26	21	25	26	20	38	51	31	96	200	53
Si*	10	18	42	^{c}	36	45	2.0	16	44	1.3	19	14	18
K	20	14	17	31	8.4	13	18	11	14	15	14	42	9.6
Mg	2	13	10	13	22	14	13	28	14	28	3.9	11	4.3
Ti*	2	6.6	11	6.7	5.9	9.4	6.3	10	14	6.4	5.2	16	4.3
P*	40	3.5	2.0	6.4	1.7	1.9	2.1	0.43	0.0085	1.2	0.57	1.7	0.77
Na	2	3.1	7.0	2.4	10	6.9	5.1	21	27	25	3.7	4.6	2.1
B	2	1.9	4.8	0.31	0.67	4.8	0.065	1.5	5.0	0.065	2.1	2.0	2.0
Sr	1	1.4	1.0	0.76	1.3	1.1	0.72	2.6	2.4	2.4	0.39	0.41	0.42
Ba*	1	1.4	3.9	1.2	3.1	4.3	1.1	5.5	17	18	2.1	1.6	0.61
Mn*	1	0.71	0.78	1.1	0.79	0.74	0.66	0.69	0.69	0.95	0.12	0.36	0.11
Cr*	10	0.17	0.088	0.83	0.056	0.11	0.37	0.30	0.15	0.29	0.17	0.32	0.097
Cu*	2	0.11	0.16	0.088	0.12	0.14	0.094	0.14	0.33	0.19	0.10	0.13	0.068
Zn*	3	0.077	0.097	0.31	0.062	0.094	0.22	0.046	0.17	0.40	0.31	0.31	0.28
Co*	2	0.027	0.036	0.042	0.030	0.029	0.033	0.045	0.055	0.054	0.065	0.11	0.041
Ni*	5	0.026	0.095	0.092	0.037	0.045	0.074	0.12	0.077	0.069	0.11	0.18	0.074
Pb*	10	^{c}	0.022	0.18	0.00056	0.0062	0.15	0.0060	0.11	0.16	0.036	0.081	0.0075
Mo*	5	^{c}	^{c}	0.050	^{c}	^{c}	0.017	^{c}	0.0093	0.026	^{c}	^{c}	^{c}
Be*	2	^{c}	^{c}	0.0015	^{d}	^{d}	^{c}	^{c}	^{c}	0.00078	0.0050	0.0029	0.0074
% elements analyzed of total sample mass		7.7	28		7.2	38		2.9	51		13	34	—

DL = Detection Limit;
* = Background correction was necessary;
^{a} = Units are in μg/g;
^{b} = Units are in μg/m^3;
^{c} = Below detection limit;
Note: The values for Si and B are low.

and if Si is already present as a non-volatile "soluble" silicate. ICP–AES values are used as the bases of the data quoted in Table III which gives the levels of the elements found in the stack emissions, coals and fly ashes collected daily at the Beckjord power plant (Eastern), the Dave Johnston power plant (Western 1a and 1b) and the Jim Bridger power plant (Western 2). It is apparent that aluminum, calcium, iron, potassium and titanium predominate in all the samples in that approximate order, ignoring the level of silicon. It is also clear that the stack emission from the high sulfur coal contained fourteen- to fifty-fold the total quantity of metals in the low sulfur coals. These figures are deceptive since each plant was operated at a different power level, and there are considerable variations in daily coal burning rates and coal-types.

Levels for Si and B will be ignored for subsequent discussion because the levels for these two elements quoted in Table III do not reflect the total values for these elements.

To assess element depletion or enrichment in the fly ash and stack emission compared with the original coal, the data were treated in three ways: Firstly, the most abundant element was selected to be the reference element and its concentration in (μg/g) or (μg/m^3) was arbitrarily designated as the 100 percent abundance. Aluminum was thus the chosen reference element. The relative abundances of the other elements were then calculated. Therefore, an element of similar relative abundance in both stack emission and coal behaves analogously to aluminum. The relative abundances for the coal, fly ash, and stack emission for the high sulfur Eastern coal are shown in Figure 1. Since changes of less than 20 percent are typical of daily chemical variation in the same type of coal,[24,25] this suggests a basis to assess enrichment or depletion relative to the original coal. Be, Mo, P and Pb were thus enriched in all stack emissions; K and Zn were also enhanced in all Western emissions. The major advantage of this criterion is that the stack emission weight does not have to be found and any analytical short-comings are the same in the quantitation of any one element, this lessening the effect of the latter.

A second way to assess element enrichment or depletion in stack emissions is to calculate the total amount of each element emitted per unit weight of stack emission collected relative to the weight of the element per unit weight of coal. The mass of each element emitted per day was calculated from Table III and the standardized daily stack flow rate (Table I). This was divided by the mass of the appropriate element in the original coal burnt per day using the burn-rate and the metal content of the coal. The enrichment factors or emission efficiencies for the elements are tabulated in Table IV in order of approximate efficiency. The most volatile elements according to this criterion were Mo, Pb, Be and Zn in all

TABLE IV

Approximate relative emission order of the elements of table III when compared with their levels in the original coals

Element	% Emission efficiency based on elemental content in coal*			
	Western 1a × 10^3	Western 1b × 10^3	Western 2	Eastern 1
Mo	$>5600^{a}$	$>2900^{a}$	$>6.8^{a}$	^{b}
Pb	$>980^{c}$	1400	3.7	0.023
Be	$>430^{d}$	^{b}	$>0.51^{d}$	0.16
Cr	9.7	37	0.13	0.062
Zn	7.9	20	1.2	0.10
Ni	7.1	11	0.079	0.075
K	4.4	12	0.18	0.078
Co	3.1	6.1	0.16	0.069
Mn	3.0	3.9	0.20	0.099
Ti	2.0	5.9	0.086	0.092
Mg	2.0	3.2	0.13	0.12
Al	2.0	5.5	0.14	0.11
Fe	1.9	4.3	0.11	0.061
Cu	1.6	4.5	0.19	0.074
Ca	1.5	3.0	0.13	0.12
Na	1.5	2.8	0.16	0.063
Sr	1.0	3.1	0.13	0.12
P	0.36	6.6	0.36	0.15
Ba	0.18	1.9	0.43	0.11

[a,c,d] Calculated assuming detection limits of 5, 10 and 2 ppb for Mo, Pb and Be, respectively.

[b] Level in stack emission is below detection level.

*Based on μg element/g stack emission divided by μg element/g coal multiplied by 100.

Western samples and Be, P, Ca and Mg in the Eastern emission. The efficiency of the electrostatic precipitation process was at least 93% with average efficiencies between 99.9 to 99.99%. Qualitatively these results are similar to those using aluminum as reference element. This is because Al is not much enhanced in the stack emission relative to its original coal.[25]

The third and preferred method to assess enrichment or depletion in stack emissions takes account of the fact that the emission rate is a function of the power of the unit of the stack.

Though the units of the Dave Johnston and Beckjord plants sampled were of approximately the same power (Table I), the Jim Bridger plant utilized a unit four times more powerful than these. The emission data from Table III is expressed in kg/day/1000 MW in Table V, assuming a linear relationship between power and emission rate. The data for the Dave Johnston plant from which two samples were taken have been expressed as ranges for each element. The approximate abundance order of the elements is arranged according to the high value of this range. The total quoted in Table V for the Western 1 plant is the average. It can be seen that the normalized emission from the Eastern plant is 15 to 40 times those from the Western plants. All the associations for each power plant noted above still hold since relative associations only were discussed.

The above conclusions, while valid overall, are not very representative of the events occurring during sample collection. It might be expected that the amount of condensate collected by successive impingers of the sampling train should decrease if material of the same volatility is being sampled. If the amount collected in each impinger is normalized with respect to the total mass recovered for each element from all impingers, the percentage in each successive impinger for each element should also decrease. For the Eastern emission, this in fact did occur, all elements save Pb being collected with 92±1%, 6±1 and 2.0±0.6 efficiencies in impingers 1, 2 and 3 respectively. The respective figures for Pb were 71, 24 and 5%. Collection of the Western 2 emission also occurred generally as expected, the average collection except for Bi, Be, and Pb being 58±5, 38 ±4 and 4±1, respectively. The respective figures for Bi, Be, and Pb were 39, 55, 6; 100, 0, 0; and 45, 49, 6.

The respective average collection for the elements in the Western 1a sample except for Be, Cu, Mo, Pb, and Zn were: 55±6, 26±4 and 19±5. The respective figures for Be, Cu, Mo, Pb, and Zn were: 0, 0, 0; 33, 3.3, 63; 21, 41, 38; 38, 35, 27; and 48, 8.3 and 44, respectively. The respective average collection for the elements in the Western 1b sample were very similar to those for the Western 1a sample and, except for Be, Ca, Cu, and Na, were: 58±5, 22±4 and 20±3. The respective figures for Be, Cr, Cu, and Na, were: 0, 0, 0; 51, 22, 28; 68, 1.5, 31; and 74, 15, and 12. The anomalous collections documented above for Cu and Zn in Western 1a, and Cr and Cu in Western 1b imply the existence of multiple chemical species of differing volatilities; Ba and Pb are merely more volatile than expected compared with the general pattern for Western 2. These effects imply that chemical speciation is important in evaluating collection efficiency for the condensate. This is also related to the power of the stack

DISCUSSION

It is evident that ICP-AES analysis will allow sensitive, multielement quantitation of stack emission condensates, coals, and fly ash. Nadkarni[46] has also reached similar conclusions for ASTM-standard coals using a similar hydrofluoric acid digestion. The use of the Parr-bomb technique ensured the retention of Si, and probably B in that study. It is evident also that the metal content of the stack emission can be related to that of of the coal (Fig. 1).

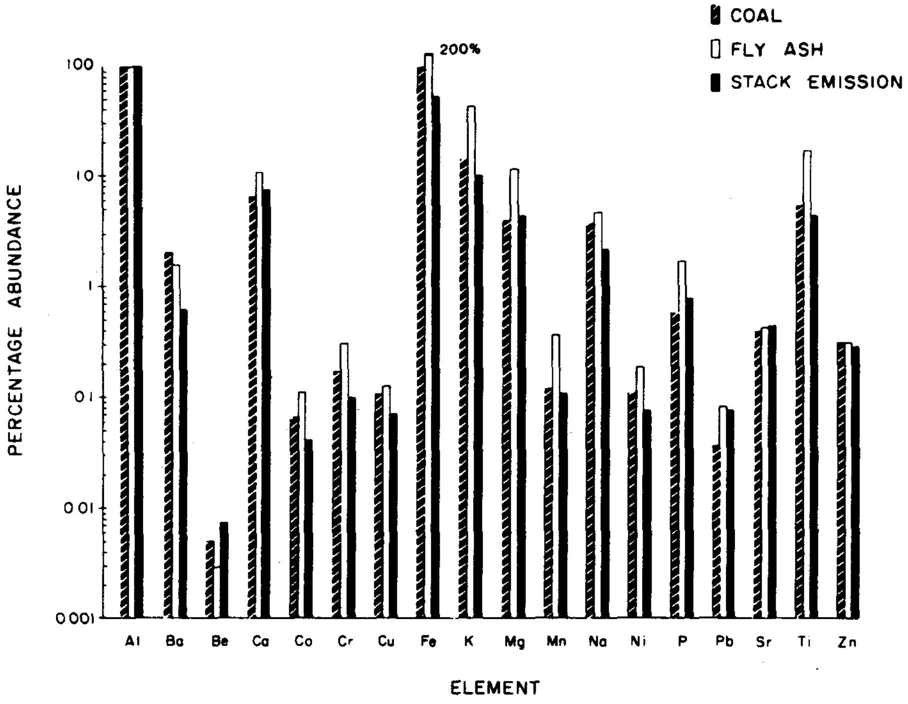

FIGURE 1 Comparison of relative abundance with respect to aluminum (expressed as μg aluminum/g sample) of some metals contained in the coal, fly ash, and stack emission of the Beckjord power plant utilizing eastern bituminous coal. The fly ash figure for iron (Fe) extends to 200%.

The direct measurement of the metal content of stack emissions from coal-fired power plants equipped with electrostatic precipitators has been previously reported by only three sets of investigators. Gladney *et al.*[32] collected in-stack samples by cascade impaction and measured the metal content by neutron activation analysis. However, not many metals were quantitated. Ondov *et al.*[24,25] have published data derived from neutron activation analysis of the emissions of two conventional Western power plants (Western Station 1 and 2 in Table V), and the U.S. EPA has similarly obtained the metal content of the emissions of a Midwest Station (Midwest Station 1 in Table V). The emission rates found by the last two investigators, along with those of the present study, have been expressed in kg/day/1000 MW units to facilitate comparison with our results (Table V). The data have been recalculated from the original data published by Ondov *et al.*[24,25] and from our own data assuming a linear relationship between power and emission rate.

TABLE V

Comparison of daily stack emission rates (kg/day/1000 MW) for elements emitted from various coal-burning power plants equipped with electrostatic precipitators (a = below detection limit; — = not measured; NAA = Neutron Activation Analysis). Emission rate from utilized coal (kg/day/1000 MW).

	Results from this study			Literature values	Values Western[24,25]	
	Western 1	Western 2	Eastern	Midwest[26]	1	2
Al	35–74	130	2900	440	2200	44
Ca	23–50	82	210	760	470	30
Fe	7.2–15	41	1500	140	510	22
K	11–13	19	280	—	130	5.9
Mg	4.5–9.3	36	130	110	190	—
Na	3.8–8.3	61	33	—	310	17
Ti	2.4–4.6	8.3	130	30	120	3.3
P	1.5–2.3	1.5	22	—	—	—
Ba	0.43–0.78	23	18	< 3.7	110	1.5
Cu	0.31–0.69	0.24	2.0	1.7	a	—
Mn	0.38–0.54	1.2	3.1	2.5	5.7	0.062
Sr	0.27–0.54	3.2	24	—	12	0.75
Cr	0.28–0.29	0.38	2.8	8.1	1.3	0.11
Zn	0.11–0.17	0.52	8.3	1.2	6.2	0.22
Pb	0.062–0.11	0.21	0.22	0.80	—	—
Ni	0.032–0.055	0.090	2.2	4.1	a	—
Co	0.015–0.025	0.071	1.2	0.20	0.33	0.014
No	0.012–0.018	0.034	a	0.40	0.90	0.011
Be	≦ 0.00054	0.0010	0.22	< 0.06	0.10	a
TOTAL	140	380	5900	1500	4000	124
Method of Analysis	ICPAES	ICPAES	ICPAES	NAA	NAA	NAA

The emissions from Western Station 1 using low sulfur sub-bituminous coal[24,25] are most similar to those measured for the Eastern plant of the present study which burned high sulfur Eastern bituminous coal (Table V). The emission from the Eastern coal relative to that for Western Station 1 was enriched in Be, Co, Cr, Ni, Fe, K and Sr but was deficient in Ba, Ca, Mn and Na. The levels calculated for Western Station 2 which burnt low sulfur bituminous coal (Table V), are very similar to those reported for Western 1a and 1b of the present study which utilized low sulfur sub-bituminous coal. The Western 1a and 1b emissions were enriched in Cr, K and Mn but were deficient in Ba, Fe, Na, Sr and Zn compared with the emission of Western Station 2. The emission from Western 2 of the present study (Table V) which used low S sub-bituminous coal is intermediate in metals content between Western Stations 1 and 2. 'The emission profile from Midwest Station 1 using low S sub-bituminous coal did not resemble the profile for any of the other power plants in Table V. Clearly the power of the stack unit is not the only factor that determines the metal composition of stack emissions. The variability of the trace element profile can be traced to a number of factors. For example, there is a clear dependence of coal type and the amount of S; the extent of coal cleaning may remove up to 67, 63, 76, 68 and 61% of As, Pb, Mn, Hg and Se respectively before combustion;[33] intrusions of clay minerals in the original coals, particularly kaolinite, quartz and $CaCo_3$ in its various forms, may account for the variation of Ca in the emissions as has been noted also for these elements in fly ash;[12] the elemental redistribution and partitioning during combustion varies according to the particular power plant configuration and also depends on the high temperature reactions of the coal compounds; the representativeness of the sample and the appropriateness of the analytical methods are also important (for example, the digestion method utilized here is clearly inappropriate for Si).

Very little is known about the chemical species actually present in stack emissions. As temperatures drop in the stack, recondensation occurs probably via heterogeneous nucleation processes with the most volatile oxides, sulfides, sulfates, carbonates, silicates and phosphates tending to be discharged to the atmosphere through the electrostatic precipitators if particle size is less than 10 microns in diameter. However, the non-uniformity of the collection of certain elements by the impinger train used in this study (e.g., for Pb, Zn, Cu, Cr noted above) is an indication that speciation is important. Some recent work on the effect of speciation in coals on the volatility of selected elements also supports this view.[35] For example, volatile arsine and nickel tetracarbonyl have been postulated to be formed in stack emissions.[36] Be, B, Cl, Cr, Co, Ge, Mg, Mn, Hg, N, Se, Na, Sr, S, Ti and V are thought also to be present partially as organic species.[37] Anderson and Smith[39] estimated that 97% of the Hg in coal is lost to the atmosphere. Bertine and Goldberg[40] postulated that As, Hg, Cd, Sn, Sb, Pb, Zn, Tl, Ag and Bi were enriched twenty-fold in the stack emission compared compared with their level in coal. Lead and zinc were certainly more volatile relative to the original coal that the other elements quantitated in the present study (Table IV).

Table VI compares the metal content of the coal and fly ashes with typical literature values.[6] Most of the figures for metals in coal and fly ash are in the usual range. However in coals, Ba and Mg contents are higher than expected; Na and Mo concentrations were lower. For the fly ashes, only Ba was enhanced above the typical range. As expected, because of

TABLE VI

Comparison of metal contents (μg/g) of coals and fly ashes

	Coal			FLY ASH		
	Typical	This study		Typical	This study	
Element	values*	Western	Eastern	values*	Western	Eastern
Al	3000–29000	9700–28000	50000	1000–170000	100000–140000	84000
Fe	2300–16000^{6},^{42}	3700–6000	48000	10000–290000	27000–52000	17000
Ca	2400–5700	6300–26000	3300	1100–220000	45000–61000	9000
K	120–4200	1100–11000	7000	400–76000	11000–14000	9400
Na	600–2400^{6,42}	890–2000	1900	100–20000	7200–28000	3900
Ti	210–6000	970–1900	2600		11000–14000	14000
Mg	1000–1300	2800–20000	2000	400–76000	11000–14000	9400
P	400^{b}	42–980	290	400–8000	9–2600	1400
Ba	70–150^{6,42}	390–650	1000	110–10000	4000–17000	1300
Sr	84–130	270–410	200	60–3900	1100–2500	340
Mn	22–100^{6,42}	64–1100	59	58–3000	720–1100	300
Cr	2–34	12–30	87	10–1000	90–160	260
Zn	8–31	4.5–22	150	50–1300	100–180	260
Ni	2–26	7.2–12	55	6.3–4300	64–98	150
Cu	19^{6}	13–240	51	14–2800	170–340	100
Pb	2–16^{6,42}	0.58–0.61	18	3.1–5000	9–120	68
Co	0.60–7.0	4	33	7–520	38–57	93
Mo	3^{b}			7–160	10	
Be			2–5			2–4

*Data unless marked originate from ref. 42.

the hydrofluoric acid digestive step, the silicon content in the fly ash was only 1 to 6 percent instead of the 20.5 percent reported by Nadkarni.[46] An excellent review on the environmental and health impact of fly ash, as well as the metal content of fly ash, coal and stack emissions is available.[6] A recent study[42] has examined the metal content of some NBS standard bituminous and sub-bituminous coals, by neutron activation analysis. ICP-AES has also been utilized in another study on the metal content of coal.[46]

The results reported in this paper may not be representative of day to day functioning of power plants. However, the close correspondence of the Western 1a and 1b samples taken on consecutive days implies that the techniques employed here do lead to consistent results and may be expected to apply over longer surveillance periods.

It might be noted that the finer particles of precipitator fly ash have been shown to be weakly mutagenic whereas coarser particles in the hopper fly ash were not.[20] However, there is some controversy on the degree of mutagenicity of the precipitator fly ash.[19]

Certain compounds containing As, Cd, Cr and Ni have been reported as human carcinogens.[41] Inhalation has been designated as a significant portal of entry to the body for these compounds. Carcinogenicity in experimental animals has also been reported[41] for Be (as BeO, $BeHPO_4$), Cd (as Cd, $CdCl_2$), Co (as Co, CoS), Cr (as $CaCrO_4$, $PbCrO_4$), Fe (iron-carbohydrates), Mn ($MnSO_4$, Mn-diacetyl acetone), Ni (as Ni, Ni_3S_2, $Ni(CO)_4$), Pb (as $Pb_3(PO_4)_2$, Pb $(CH_3COO)_2$), Ti (as $Ti(C_5H_5)_2$) and Zn (as $ZnCl_2$). Of these, Be, Cr and Ni induced cancers by inhalation. Chemical speciation of airborne metals is thus an important variable to be considered in the initiation of toxic effects. It is likely that some of the compounds noted here may be found in stack emissions.

Stack emissions are known to contribute to the evolution of acid rains although the extent of this contribution has not been assessed.[43,44] Inductively coupled plasma analysis of freshly fallen rain to evolve metal fingerprints in the manner given in this paper may provide insight into this question.

Acknowledgement

This study was funded by U.S. EPA No. 68-03-2601 and U.S. PHS Grant ES-00159. Thanks go to Jim Boiano and James Boyle for their technical assistance in the atomic absorption determinations. PEDCO Environmental Corporation collected the stack emission samples.

References

1. A. E. Vandegrift, L. J. Shannon and P. G. Gorman, *Chem. Eng. (New York)* **80,** 107 (1973).
2. P. E. Morrow, *Health Phys.* **12,** 173 (1966).
3. *U.S. Bureau of Mines, Minerals Yearbook, Vol.* 1, *Metals, Minerals and Fuels,* U.S. Govt. Printing Office, Washington, D.C. (1974).
4. *Interagency Task Force on Coal, Project Independence, Federal Energy Administration,* Task Force Report, (1975).
5. M. L. Lee, D. W. Later, D. K. Rollins, D. J. Eatough and L. D. Hansen, *Science* **207,** 186 (1980).
6. A. L. Page, A. A. Elseeni and I. R. Straughan, *Residue Rev.* **71,** 83 (1979).
7. W. S. Lyon, *Trace Element Measurements at the Coal-Fired Steam Plant,* CRC Press, Cleveland, Ohio, (1977).
8. C. Block and R. Dams, *Environ. Sci. Technol.* **9,** 146 (1975).
9. C. Block and R. Dams, *Environ. Sci. Technol.* **10,** 1011 (1976).
10. R. L. Davison, D. F. S. Natusch, J. R. Wallace and C. A. Evans, Jr., *Environ. Sci. Technol.* **8,** 1107 (1974).
11. J. W. Kaakinen, R. M. Jorden, M. H. Lawasani and R. E. West, *Environ. Sci. Technol.* **9,** 862 (1975).

12. G. L. Fisher, D. P. Y. Chang and M. Brummer, *Science* **192,** 553 (1976).
13. V. E. Swanson, *Appl. J. Southwest Energy Study,* U.S. Dept. Int. Open File Report (1972).
14. V. E. Swanson, J. M. Medlin, J. R. Hatch, S. L. Coleman, G. H. Wood, Jr., S. D. Woodruff and R. T. Hildebrand, U.S. Dept. Int., Geol. Survey, Open File report 76–468 (1976).
15. D. J. Swaine, in D. D. Hemphill (Ed.); *Trace Substances in Environmental Health* **XI,** 107 (1977).
16. A. K. Furr, T. F. Parkinsen, R. A. Hinrichs, D. R. Van Campen, C. A. Bache, W. H. Gutenmann, L. E. St. John, Jr., I. S. Pakkala and D. J. Lisk, *Environ. Sci. Technol.* **11,** 1104 (1977).
17. C. Aranyi, F. J. Miller, S. Andres, R. Ehrlich, J. Fenters, D. E. Gardner and M. D. Waters, *Environ. Res.* **20,** 14 (1979).
18. W. J. Birge, *DOE Symp. Ser.* **48,** 219 (1977).
19. H. E. Kubitschek and L. Venta, *Environ. Mutagen.* **1,** 79 (1979).
20. G. L. Fisher, C. E. Chrisp and O. G. Raabe, *Science* **204,** 879 (1979).
21. W. A. Korfmacher, D. F. S. Natusch, D. R. Taylor, G. Mamantov and E. L. Wehry, *Science* **207,** 763 (1980).
22. A. W. Andren, B. G. Blaylock, E. A. Bondietti, C. W. Francis, S. G. Hildebrand, J. W. Huckabee, D. R. Jackson, S. E. Lindberg, F. H. Sweeton, R. I. Van Hook and A. P. Watson, in: *Ecology and Analysis of Trace Contaminants,* National Science Foundation, ORNL-NSF-EATC-11, pp. 61–104 (1974).
23. W. H. Zoller, E. S. Gladney, G. E. Gordon and J. J. Bors, in D. D. Hemphill (Ed.): *Trace Substances in Environmental Health* **VIII,** 167 (1974).
24. J. M. Ondov, R. C. Ragaini and A. H. Biermann, *Environ. Sci. Technol.* **13,** 946 (1976).
25. J. M. Ondov, R. C. Ragaini and A. H. Biermann, *Environ. Sci. Technol.* **13,** 598 (1979).
26. U. S. EPA: *Coal-fired Power Plant, Trace Element Study. Vol.* 1. *A Three Station Comparison. Rocky Mountain-Prairie Region.* Region VIII, Denver, CO (1975).
27. D. H. Klein and P. Russell, *Environ. Sci. Technol.* **7,** 357 (1973).
28. G. R. Bradford, A. L. Page and I. R. Straughan, in D. C. Adriano and I. L. Brisbin, Jr., (Eds.): *Environmental Chemistry and Cycling Processes.* Proc. Symp. Augusta, GA, April 28–May 1, 1976. DOE Symposium Ser. **45,** CONF-760429, pp. 383–393 (1978).
29. A. M. Hartstein, R. W. Freedman and D. W. Platter, *Anal. Chem.* **45,** 611 (1973).
30. L. E. Kopito, *Atomic Absorption Methods Manual, Volume III,* Jarrell–Ash Division, Fisher Scientific Company (1970).
31. T. E. Cody and V. J. Elia, *Ann. Rep. Center Study Human Environ.* Dept. Environ. Health, Kettering Lab., Univ. Cincinnati, p. 69 (1978/1979).
32. E. S. Gladney, J. A. Small, G. E. Gordon and W. H. Zoller, *Atmos. Environ.* **10,** 1071 (1976).
33. C. T. Ford, R. R. Care and R. E. Bosshart, *Preliminary Evaluation of The Effect of Coal Cleaning on Trace Element Removal.* Trace Element Program, Report No. 3, Bituminous Coal Research Inc., 350 Hochberg Rd., Monroeville, PA, (1976).
34. J. Bern, in *Land Application of Waste Materials,* Soil. Conserv. Soc. Amer. Ankeny, Iowa, pp. 226–248 (1976).
35. B. T. G. Ting and S. E. Manahan, *Environ. Sci. Technol.* **13,** 1537 (1979).
36. D. W. Koppenaal and S. E. Manahan, *Environ. Sci. Technol.* **10,** 1104 (1976).
37. A. Attari, M. Mensinger and J. Pau, U.S. EPA Agency Report, EPA-600/2-76-259, Washington, D.C. (1976).
38. S. E. Manahan, *Environmental Chemistry,* 3rd Ed., Willard Grant Press, Boston, Chapter 4 (1979).
39. W. L. Anderson and K. E. Smith, *Environ. Sci. Technol.* **11,** 75 (1977).

40. K. K. Bertine and E. D. Goldberg, *Science* **173,** 233 (1971).
41. F. W. Sunderman, Jr., *Biol. Trace Element Res.* **1,** 63 (1979).
42. M. S. Germani, II. Gokmen, A. C. Sigleo, G. S. Kowalczyk, I. Olmez, A. M. Small, D. L. Anderson, M. P. Falley, M. C. Gulovali, C. E. Choquette, E. A. Lepel, G. E. Gordon and W. H. Zoller, *Anal. Chem.* **52,** 240 (1980).
43. H. M. Liljestrand and J. J. Morgan, *Environ. Sci. Technol.* **12,** 1271 (1978).
44. G. E. Likens, R. F. Wright, J. N. Galloway and T. J. Butler, *Sci. Amer.* **241,** 43 (1979).
45. *Federal Register* **42,** (160), August 18, 1977. Method 5.
46. R. A. Nadkarni, *Anal. Chem.* **52,** 929 (1980).
47. F. W. Chapman Jr., G. G. Marvin and S. Y. Tyree Jr., *Anal. Chem.* **21,** 700 (1949).