

## TRACE ELEMENT ANALYSIS OF COAL BY NEUTRON ACTIVATION

Dean W. Sheibley

National Aeronautics and Space Administration  
 Lewis Research Center  
 Cleveland, Ohio

## INTRODUCTION

This report presents the technology methods used at the NASA Plum Brook reactor (PBR) to analyze coal by neutron activation analysis. The work was performed for the Environmental Protection Agency (EPA) Division of Air Surveillance at Research Triangle Park, North Carolina, by the NASA Plum Brook reactor at Sandusky, Ohio, under an interagency agreement. Unfortunately, the work was terminated in January 1973 when the Plum Brook reactor was closed.

The general scheme of analysis - sample preparation, irradiation, and sample counting - is described. The discussion of data reduction includes the computerized method, interference corrections, and the precision and accuracy of the method. Some typical trace element results are given for coal, fly ash, and bottom ash. The manpower requirement for the analysis of 1000 samples per year is stated.

## THE ANALYSIS SCHEME

Figure 1 shows the overall analysis scheme used at PBRF to analyze coal and fly ash samples by neutron activation analysis (NAA). (These same techniques and methods, with only slight modification, were used for the NAA of kerosene, jet fuel, gasoline, fuel oil, residual oil, ore, air particulates on filters, bottom ash, sand, clam tissue, corn, cement, limestone, stack scrubber water, crab shells, and river water.)

The basic procedure used two aliquots of the sample. One aliquot was encapsulated in a polyethylene vial, the other in a synthetic quartz (Suprasil) vial. The polyethylene vial, containing 50 to 100 milligrams of coal (10 mg or less of fly ash), was irradiated for 5 minutes in a thermal neutron flux of  $1.5 \cdot 10^{14}$  n/cm<sup>2</sup>/sec. Then the irradiated sample was counted at decay times of ~5 minutes, ~30 minutes, and 24 hours. The quartz vial was irradiated for 12 hours in the same flux and counted at about 3 weeks decay.

Samples were counted on a 4096 channel gamma ray spectrometer using a Ge (Li) detector with a crystal diameter of 35 mm and length of 27 mm. Acceptable counting distances ranged from 3 to 40 cm, with detector dead time restricted to <20% whenever possible. The detector resolution was 3 keV with linearity adjusted to 1 keV/channel and maintained at  $\pm 1$  channel or less.

## DATA REDUCTION

Altogether there were two irradiations associated with each pollution sample, and four counts - 5 minutes, 30 minutes, 24 hours, and 3 weeks decay. Each count of each aliquot produced a paper tape. Each tape, along with information regarding decay time, count time, flux level, sample weight, counting distance, and other parameters was processed through the data reduction code "SPECTRA."<sup>(1)</sup> Computing time on an IBM 360 Mod 67 was under 1 minute for all four tapes associated with one sample. Data were reported to EPA as parts per million of each trace element in the sample.

## INTERFERENCE CORRECTIONS

EPA designates the elements Hg, Se, As, as "very hazardous." As a result, we devoted much attention to the accurate determination of these four elements by NAA. We found that, in coal, both selenium and ytterbium interfered with the detection of mercury; ytterbium interfered with selenium; and bromine and antimony interfered with arsenic.

The appendix to this paper describes how factorial experiment design techniques were used to derive empirical correction factors needed for the accurate determination of Hg, Se, and As.

## PRECISION AND ACCURACY

Table 1 shows the standard deviation and the range of counting precision associated with the determination of trace elements in coal. The standard deviation is based on five aliquots.

Table 2 provides information on the accuracy of the NAA methods. Results of NAA of NBS standard reference materials (trace elements in a glass matrix) are compared with certified and interim NBS values. Other elements reported to EPA were frequently checked with homemade standards and with standards submitted by EPA.

## TYPICAL TRACE ELEMENT RESULTS

Tables 3.1 to 3.4 show the form of computer outputs typically obtained, one for each of the four spectra associated with one sample. The data include the PBR sample number, the EPA identification number, and the input data required for the computerized data reduction. The third column shows the 56 elements that were routinely reported. Column four gives the results in ppm, and column 5 gives the standard deviation at 1 $\sigma$  in ppm.

Typical results are tabulated in table 4 for seven coal samples, bottom ash, and fly ash. The results are given in ppm. The elements are listed along with the isotopes actually detected. Examination of the data shows that calcium, cerium, iron, aluminum, barium, potassium, manganese, sodium, rubidium, tin, titanium, thorium, uranium, vanadium, and zirconium are concentrated in fly ash. An additional comment regarding uranium and thorium: these elements are naturally radioactive and are  $\alpha$ -emitters. For each ton of coal burned, the potential hazard exists of emitting 0.3 curies of  $\alpha$ -activity, based on 1 ppm of uranium in coal.

No element in table 4 shows a higher concentration in the bottom ash than in the fly ash.

## THE ANALYSIS CAPABILITY

The analysis capability developed at the Plum Brook reactor was geared to analyze 1000 samples per year as a part time effort. The program was also geared to developing the technology to handle and irradiate a large variety of pollution related samples with a minimum of manpower. During a typical work week, 24 samples were irradiated, counted, and reported. Total manpower expended averaged 3.0 to 3.5 hours per sample. Computer running time amounted to approximately 1 minute per sample with 56 elements reported.

## CONCLUDING REMARKS

The trace element analysis of coal using NAA has been shown to be an accurate, reliable, and instrumental method of analysis. The associated technology was also developed to permit the analysis of up to 56 trace elements in each of 1000 samples

per year as a part-time effort. Computerized data reduction reduced the total manpower required to 3.0 to 3.5 hours per sample.

#### APPENDIX - INTERFERENCE CORRECTIONS FOR MERCURY, SELENIUM, AND ARSENIC

by Anne Bodnar

The elements Hg, Se, As, and Cd are designated as "very hazardous" by EPA. This appendix describes the method used to derive the complex correction factors required to achieve an accurate determination of Hg, Se, and As by NAA. Cadmium did not require any special interference corrections.

We detected an accuracy problem with the determination of Hg in coal. A count at 5 to 6 weeks decay time produced a Hg result ranging from 2 to 10 times smaller than the value obtained at 3 weeks decay. A correction for Se interference on Hg was being made, but, because of the similarity in the half-lives of Hg<sup>203</sup> and Se<sup>75</sup>, the low Hg results at 6 weeks decay could not be explained.

A search of the Nuclear Data Tables<sup>(2)</sup> produced another interference: 4.2-day Yb<sup>175</sup>. Not only did the 282-keV peak of Yb<sup>175</sup> interfere with Hg<sup>203</sup>, but also the 400.7-keV peak of Se<sup>75</sup> interfered with the 396-keV peak area of Yb<sup>175</sup>, which was used for the Yb correction on Hg<sup>203</sup>. In addition, another Yb isotope, 32-day Yb<sup>169</sup> interfered with the 264-keV peak area of Se<sup>75</sup>, which is used in the correction on Hg<sup>203</sup> (peak area at 279 keV). These discrepancies were not eliminated by using theoretical corrections.

Finally, the problem was resolved by irradiating standards and mixtures of standards in a factorial experiment. The experiment design was a full factorial experiment with three variables (Hg, Se, Yb) at two levels, with replication, and with a center point added to test higher order effects. The high level was selected as 100 micrograms (µg), the low level as 10 µg. Table A-1 shows the treatments that were used.

Regression analysis on the data was used to estimate the coefficients in a predictive model equation. The dependent variable was chosen as the difference between the computer calculated value for Hg (or Se or Yb) and the true value. Independent variables were the other two elements plus plausible interactions (e.g., the interaction of Se-Yb on Hg). The coefficients derived for the predictive equations served as the basis for the empirical correction of Yb on Se and vice versa, and Yb-Se on Hg. Table A-2 compares the theoretical correction factors with the final form of the corrections based on the empirical data. A special subroutine was added to the SPECTRA computer program. The program was then tested by irradiating and analyzing other known samples. The calculated values agreed with the known sample contents. The method now allows us to determine Se and Hg in the presence of interferences which may be ten times greater in quantity.

This same technique has been used to determine arsenic in the presence of bromine and antimony.

#### REFERENCES

1. G. A. Borchardt, G. E. Hoagland, and R. A. Schmitt, J. Radioanalyt. Chem., **6**, 241 (1970).
2. Anon., "Nuclear Data Tables," Academic Press, New York, N.Y.

TABLE A-1

Treatment	Se	Hg	Yb	
1	-1	-1	-1	(-1) indicates low level, 10 $\mu$ g
2	+1	-1	-1	
3	-1	+1	-1	(+1) indicates high level, 100 $\mu$ g
4	-1	-1	+1	
5	+1	+1	-1	CP indicates $\left(\frac{\text{High level} + \text{low level}}{2}\right)$
6	-1	+1	+1	
7	+1	+1	+1	
8	+1	-1	+1	
Replicates				
4	-1	-1	+1	
7	+1	+1	+1	
8	+1	-1	+1	
Center point	CP	CP	CP	

TABLE A-2

## 1. Theoretical corrections for Se and Yb interferences on Hg

$$1. A_c = A_u - 0.0369 X$$

$$2. B_c = B_u - 0.118 A_c$$

$$3. D_c = D_u - 0.959 B_c - 0.387 A_c$$

## 2. Empirical form of Se and Yb correction factors for interference on Hg

$$1. A_c = A_u - 0.0433 X$$

$$2. B_c = 0.443(B_u - 0.118 A_c)$$

$$3. D_c = D_u - 1.65 B_c - 0.387 A_c$$

where  $A_c$  = selenium 264.6 KeV area corrected for Yb<sup>169</sup>

$A_u$  = net area of selenium (264.6 KeV), uncorrected

$X$  = net area of Yb<sup>169</sup> at 177.2 KeV

$B_c$  = ytterbium 396.1 KeV area corrected for selenium (264.6 KeV)

$B_u$  = net area of ytterbium (396.1 KeV) uncorrected

$D_c$  = mercury 279.1 KeV area corrected for selenium and ytterbium

$D_u$  = net area of mercury (279.1 KeV) uncorrected

TABLE 1. - PRECISION OF EPA ROUND ROBIN COAL SAMPLE

Element	ppm	% std dev (1 $\sigma$ )	Range of counting precision at 1 std dev, %
Ti	1 312	12	10-20
V	36	11	5-10
Al	15 700	9	0.6-1
S	<30 500	50	-----
U	0.98	8	8-12
Ba	340	12	5-8
Sr	93	10	8-11
I	2.8	14	12-30
Mn	38	7	0.5
Mg	890	28	12-33
Na	370	9	2-3
Cl	750	10	2
Ca	4 070	14	8-15
Cu	14	6	3-5
As	5.9	9	10-12
Br	20.	15	9-12
K	3 500.	10	3-4
Cd	<55	23	-----
Ce	17.3	5	1-2
Se	3.8	13	25-33
Hg	0.95	10	7-40
Cr	19	4	3-5
Cs	2.6	3	8-10
Ag	<0.4	25	-----
Zr	<70	55	-----
Zn	7.5	--	33
Fe	7 520	2	1
Co	5.5	15	1-13
Sb	6.4	24	8-15
Ni	<65	31	-----

TABLE 2. - COMPARISON OF NBS STANDARD REFERENCE MATERIALS WITH PBR RESULTS

	NBS 610*/PBR	NBS 612/PBR	NBS 614/PBR	NBS 616/PBR
Antimony	---	---	(1.06)/1.1 $\pm$ .1	0.078 $\pm$ .007/0.12 $\pm$ .02
Cerium	---	(39)/37 $\pm$ 2	---	---
Cobalt	(390)/135 $\pm$ 14	(35)/31 $\pm$ 1	0.73 $\pm$ 0.02/0.59 $\pm$ .006	---
Europium	---	(36)/26 $\pm$ 1	0.99 $\pm$ .04/1.1 $\pm$ .6	---
Gold	(25)/20 $\pm$ 2	(5)/4.7 $\pm$ 1	(0.5)/1.0 $\pm$ .8	---
Lanthanum	---	(36)/35 $\pm$ 15	0.53 $\pm$ .02/<2	---
Thorium	---	37.6 $\pm$ .09/31.2 $\pm$ 1	0.746 $\pm$ .007/0.58 $\pm$ .15	0.025 $\pm$ .004/0.018 $\pm$ .002
Scandium	---	---	0.59 $\pm$ .04/0.68 $\pm$ .23	0.026 $\pm$ .012/0.020 $\pm$ .004
Silver	(254)/180 $\pm$ 80	22.0 $\pm$ .8/31 $\pm$ 7	0.46 $\pm$ .02/0.57 $\pm$ .07	---

\* NBS values in parentheses are interim values for various reasons. Others are certified values.

TABLE 3.1 - TYPICAL INPUT AND OUTPUT DATA

SAMPLE NUMBER 2685  
 ---EPAFA1280

DECAY TIME	810.	SEC.		
COUNT TIME	200.	SEC.		
SAMPLE MASS	0.4400F-01	GRAMS		
READ TIME	32.00	?		
LENGTH OF IRRADIATION TIME	300.0	SEC.		
FLUX LEVEL	0.1720F 15	NT. DEP SQ.CM. DEP SEC.		
DISTANCE	10.0CM.			
AREA OF FILTER IRRADIATED	0.000	SQ.CM.		
TOTAL AREA OF FILTER	0.000	SQ.CM.		
VOLUME OF AIR FILTERED	0.00000000	CURIC METERS		
KSIDPEA	4			
PG 2685	--- <td>RH</td> <td>0.58628274E-01</td> <td>0.68124980E-02</td>	RH	0.58628274E-01	0.68124980E-02
PG 2685	--- <td>YI</td> <td>0.32399634E 03</td> <td>0.43813904E 02</td>	YI	0.32399634E 03	0.43813904E 02
PG 2685	--- <td>V</td> <td>0.12669642E 02</td> <td>0.68239159E 00</td>	V	0.12669642E 02	0.68239159E 00
PG 2685	--- <td>AL</td> <td>0.34132515E 04</td> <td>0.44224457E 02</td>	AL	0.34132515E 04	0.44224457E 02
PG 2685	--- <td>S</td> <td>0.74391514E 04</td> <td>0.49796406E 04</td>	S	0.74391514E 04	0.49796406E 04



TABLE 3.3 - TYPICAL INPUT AND OUTPUT DATA

SAMPLE NUMBER 2654  
 ---EPAF12R0

DECAY TIME	68400.	SEC.							
COUNT TIME	1000.	SEC.							
SAMPLE MASS	0.4400E-01	GRAMS							
DEAD TIME	10.00	μ							
LENGTH OF IRRADIATION TIME	300.0	SEC.							
FLUX LEVEL	0.1720E 15	NT. DEO SO.CM. PER SEC.							
DISTANCE	3.0CM.								
AREA OF FILTER IRRADIATED	0.000	SO.CM.							
TOTAL AREA OF FILTER	0.000	SO.CM.							
VOLUME OF AIR FILTERED	0.00000000	CURIC METERS							
KSIJDDA	4								
FIG 2694	----	EPAF12R0	SM	0.69228021F	00	0.36308378E-01			
FIG 2654	----	EPAF12R0	FU	0.15409475E	00	0.23547603E-01			
FIG 2694	----	EPAF12R0	TP	0.12648592E	01	0.19465458E	00		
FIG 2694	----	EPAF12R0	AU	C <	0.21256555E	00	0.39333303E-01		
FIG 2654	----	EPAF12R0	CU	0.72891830E	01	0.35303469E	00		
FIG 2694	----	EPAF12R0	AS	0.18097029E	01	0.51812541E	00		
FIG 2694	----	EPAF12R0	RP	0.34650284E	02	0.19843575E	01		
FIG 2694	----	EPAF12R0	GA	0.17451668E	01	0.61991853E	00		
FIG 2694	----	EPAF12R0	K	0.21975392E	03	0.73871231E	02		
FIG 2694	----	EPAF12R0	LA	0.49075308E	01	0.54219289E	00		
FIG 2694	----	EPAF12R0	PT	E <	0.90368561F	02	0.69488037E	02	
FIG 2694	----	EPAF12R0	W	E <	0.14073496E	01	0.65515435F	00	
FIG 2694	----	EPAF12R0	GD	E <	0.18515747E	02	0.18053726E	02	
FIG 2694	----	EPAF12R0	CD	E <	0.59213211E	02	0.54743378E	02	
FIG 2694	----	EPAF12R0	RE	E <	0.97890139E-01		0.60177512E-01		
FIG 2694	----	EPAF12R0	MO	E <	0.65644312E	03	0.39779175E	03	



TABLE 4. - ENVIRONMENTAL PROTECTION AGENCY SAMPLES\* - COAL, FLY ASH, AND BOTTOM ASH

Element/ isotope	Coal L-14	Coal L-15	Coal L-16	Coal L-17	Coal L-18	Coal L-19	Coal L-20	Bottom ash L-21	Fly ash L-22	Fly ash L-23
Ag <sup>110M</sup>	<0.9	<0.7	<0.6	<0.6	<0.2	<0.2	<0.3	<0.2	<0.4	<0.2
Al <sup>28</sup>	17 200	8 080	13 300	12 100	10 800	6.170	27 600	67 500	89 600	99 700
As <sup>76</sup>	7.00	<1.2	4.8	<5	2.44	1.6	<6	<5	<7	<6
Au <sup>198</sup>	0.003	C.10	0.07	0.15	0.06	0.02	<0.4	<0.5	<2	<2
Be <sup>139</sup>	92	34	48	53	45	29	565	1500	1641	2370
Br <sup>82</sup>	20	3	22	19	9.0	16	<20	<15	<50	<30
Ca <sup>49</sup>	7 740	3 640	5640	<5 000	3290	1910	5960	14 300	23 200	26 200
Cd <sup>115</sup>	<300	<110	<110	<90	<200	<30	<100	<900	<1200	<2000
Ce <sup>141</sup>	21.1	8.83	16.2	13.0	10.6	8.97	28.0	71.8	104	103
Cj <sup>38</sup>	2820	1220	2760	1450	1250	2350	189	94	<200	168
Ni(Co <sup>58</sup> )	<90	<30	<80	<70	<60	<30	<20	<50	<80	<50
Co <sup>60</sup>	5.98	3.07	5.22	4.40	3.84	4.02	1.92	4.72	6.6	6.8
Cr <sup>51</sup>	24.2	18.0	21.4	19.4	19.3	12.2	5.26	14.8	22	21
Cs <sup>134</sup>	3.32	1.56	2.58	2.35	2.03	1.13	0.92	2.81	4.4	4.1
Cu <sup>64</sup>	<30	29	<20	<20	<20	<20	<50	37	57	70
Dy <sup>165</sup>	1.2	0.58	0.76	0.77	0.67	0.42	0.90	2.0	2.8	3.50
Eu <sup>152m1</sup>	0.56	0.2	0.32	0.31	.30	.18	.36	0.91	1.2	1.5
Fe <sup>59</sup>	8970	13 700	9500	10 900	11 600	4550	6150	20 000	24 400	23 600
Ga <sup>72</sup>	7.2	<2	4.0	4.2	5.5	2.9	<6	<2	<30	<30
Ge <sup>75</sup>	<70	<4	<120	<40	<150	<150	<20	<200	<300	<400
Hf <sup>181</sup>	1.05	0.50	0.81	0.65	0.60	0.42	2.28	6.50	8.5	8.7
Hg <sup>203</sup>	<0.7	<0.5	<0.6	1.91	0.16	<0.3	<0.5	<0.7	<0.9	<0.9
Gd <sup>159</sup>	<70	<60	<40	<30	<40	<20	<80	<120	<140	<400
I <sup>128</sup>	<0.2	<1	<0.5	1.8	<2	0.65	<2	<1	<2	<20
In <sup>116m1</sup>	<0.05	<0.03	<0.02	0.073	0.029	<0.01	<0.05	<0.07	<0.02	<0.07

\*The EPA could not reveal the source of these samples.

TABLE 4. - Continued. ENVIRONMENTAL PROTECTIVE AGENCY SAMPLES - COAL, FLY ASH, AND BOTTOM ASH

Element/ isotope	Coal L-14	Coal L-15	Coal L-16	Coal L-17	Coal L-18	Coal L-19	Coal L-20	Bottom ash L-21	Fly ash L-22	Fly ash L-23
Ir <sup>192</sup>	5.3	1.9	2.2	6.7	1.6	1.8	7	11	9.8	13
K <sup>42</sup>	7130	2464	3932	3748	3420	1690	1810	7170	9064	9800
La <sup>140</sup>	17.2	5.7	7.2	26	7.3	5.4	20	29	25	57
Lu <sup>177</sup>	0.58	0.36	0.42	0.32	0.35	0.22	0.51	1.23	1.6	1.8
Mg <sup>27</sup>	<450	<850	<1200	<4000	585	<600	1320	<11 000	2400	<9000
Mn <sup>56</sup>	95	53	62	49	38	25	93	300	371	422
Mo <sup>99</sup>	<600	<700	<260	<350	<300	<200	<3100	<2200	<13 000	<6000
Na <sup>24</sup>	1250	882	1070	833	757	487	2850	6080	8430	14 000
Nd <sup>147</sup>	<7	<2	<2	<5	<7	<3	<7	<10	<40	<30
Pt <sup>197</sup>	<300	<170	<160	<230	<200	<100	<1000	<700	<1400	<3200
Rb <sup>86</sup>	25.6	12.3	20.7	21.4	16.8	7.98	8.66	15.9	45	41
Re <sup>188</sup>	<0.3	<0.2	<0.2	<0.3	<0.4	<0.3	<0.5	<2	<1	<0.4
Rh <sup>104</sup>	<0.03	<0.09	<0.04	<0.2	<0.06	<0.06	<0.07	<0.3	<4	<0.3
S <sup>37</sup>	*	37 500	<53 000	<7 000	<9000	<30 000	<200 000	168 000	<200 000	<300 000
Sc <sup>46</sup>	4.56	2.67	3.84	3.42	3.17	2.07	3.02	7.42	11.4	11.7
Sb <sup>124</sup>	1.39	0.84	1.12	0.93	0.62	0.86	0.80	0.50	2.1	1.8
Se <sup>75</sup>	4.15	3.12	2.99	3.19	2.86	1.77	3.07	2.10	5.98	5.72
Sm <sup>153</sup>	2.23	0.82	1.2	1.2	1.1	0.81	1.5	3.5	4.4	4.9
Sr <sup>87m</sup>	56	<30	36	<20	<40	<20	106	<100	223	<200
Sn <sup>117m</sup>	76.5	<40	74.2	66	50	34	86	428	555	422
Ta <sup>182</sup>	0.35	0.12	0.27	0.25	0.18	0.17	0.65	1.66	2.4	2.4
Tb <sup>160</sup>	0.036	0.018	0.027	0.025	0.022	0.015	0.048	0.12	0.18	0.18
Th(Pa <sup>133</sup> )	4.19	2.16	3.23	2.84	2.84	1.73	7.49	19.1	25	25

\* Data missing.

TABLE 4. - Concluded. ENVIRONMENTAL PROTECTIVE AGENCY SAMPLES - COAL, FLY ASH, AND BOTTOM ASH

Element/ isotope	Coal L-14	Coal L-15	Coal L-16	Coal L-17	Coal L-18	Coal L-19	Coal L-20	Bottom ash L-21	Fly ash L-22	Fly ash L-23
Ti51	1680	912	608	980	908	529	893	3820	4280	3428
U239	1.5	0.96	0.82	1.14	0.82	0.68	1.3	3.7	4.7	4.9
V52	34	23	26	27	23	15	18	29	65	64
W187	<4	<0.3	<0.4	<2	<2	<2	<20	<15	<20	<30
Yb175	3.68	1.88	4.06	1.83	0.46	0.91	0.84	2.36	3.8	2.9
Zn65	264	<3000	220	148	118	<400	<2000	187	299	341
Zr95	<50	<50	<50	<40	<50	<30	107	261	400	556

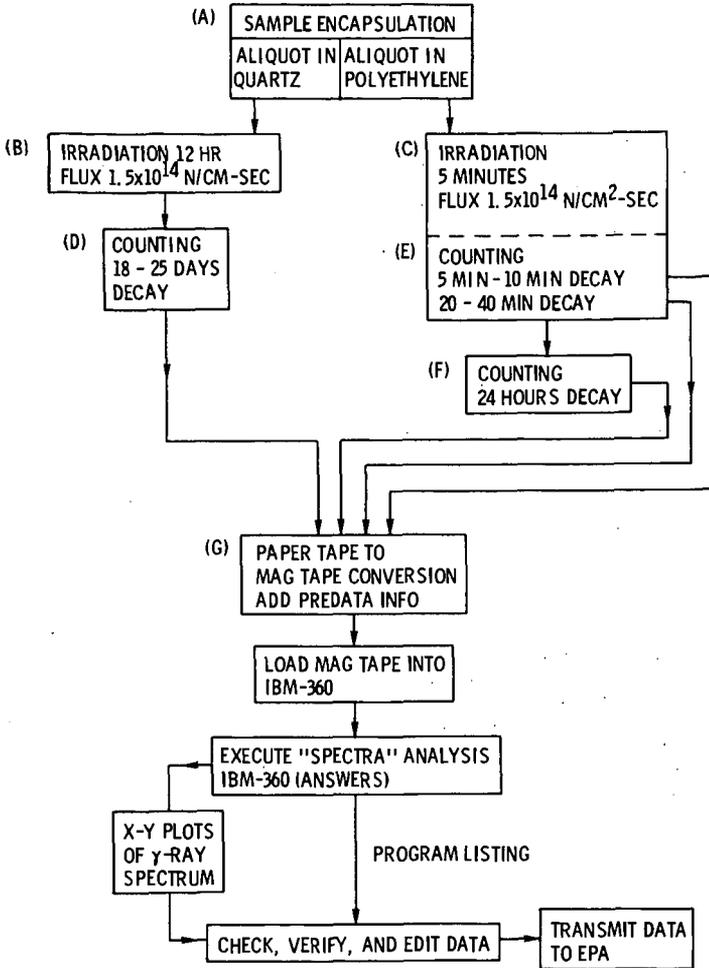


Figure 1. - Flow chart showing scheme for sample irradiation, counting, and data reduction of coal samples.

## X-RAY FLUORESCENCE ANALYSIS OF WHOLE COAL

John K. Kuhn, William F. Harfst, and Neil F. Shimp

Illinois State Geological Survey

Introduction

Recent interest in the trace element content of coal has led to the need for development of rapid, accurate analytical methods for their determination. Because X-ray fluorescence analysis has demonstrated its usefulness in the determination of major, minor, and trace elements in numerous types of materials, it was felt that this method could be extended to trace element determinations in whole coal. In the past such analyses have been seriously hampered by the lack of standard samples. However, U. S. Environmental Protection Agency sponsored research, which is being conducted in our laboratories, has generated a large number of coal samples for which trace elements have been determined by two or more independent analytical procedures (viz. optical emission, neutron activation, atomic absorption and wet chemical methods). Using these coals as standards, a X-ray fluorescence method has been developed for the determination of a number of trace and minor elements in pressed whole coal samples.

The instrument used in this project was a Phillips manual vacuum X-ray fluorescence spectrometer. All analyses for this study were made in the Analytical Chemistry Laboratories of the Illinois State Geological Survey. The work upon which this report is based was partially supported by U. S. Environmental Protection Agency Contract 68-02-0246.

Preliminary Investigation of Major and Minor Elements  
in Whole Coal and Coal Ash

Two different types of materials - coal ash and whole coal - were analyzed in this project, and sample preparation was varied accordingly.

Whole coal was ground with 10 per cent by weight of a binder and pressed into a disc, which was used as the analytical sample without further treatment. Sample preparation techniques are given in detail in Illinois State Geological Survey Environmental Geology Note 61.

It was found that two grams of coal gave a disc that was infinitely thick with respect to soft X-rays emitted by "light" elements such as Mg, Si, Al, and Ca; however, for elements "heavier" than Br, it was necessary to increase the sample weight to attain infinite sample thickness, i.e., no X-rays penetrated through the pressed coal sample.

Our use of X-ray fluorescence was originally intended for the purpose of establishing major element matrix information on coal ashes to be analyzed for trace elements by optical emission spectroscopy. Both low temperature (<150° C) and high temperature (450° C) coal ashes, prepared as described by Kuch, Gluskoter, and Shimp (1973), were used for this purpose, and the method of Rose, Adler and Flannigan (1961) was adapted for the determination of major and minor elements (Si, Ti, Al, Fe, Mg, Ca, K, and V). The instrumental parameters used for these elements are given in Table 1. To assess the validity of this procedure, a series of analyzed coal ashes obtained from the British Coal Utilization Research Association (BCURA) were analyzed along with the two types of ash prepared in our laboratories. Calibrations for these analyses were prepared from National Bureau of Standards rock standards (1B, G1, W1, No. 78, No. 79, No. 88). The values determined for the BCURA coal ashes were in excellent agreement with published results of Dixon, Edwards, Flint, and James (1964). Standard deviations were calculated for duplicate coal ash determinations. They were: Si - .0715%, Ti - .0066%, Al - .0567%, Fe - .0493%, Mg - .0178%, Ca - .0282%, K - .0123%, P - .0074%, and V - 1.3 ppm. These deviations are comparable to "Class A" wet silicate analyses and are indicative of a high degree of accuracy.

Because of these encouraging results and previous work on brown coals by Sweatman, Norrish, and Durie (1963) and Kiss (1966), which indicated that major and

minor elements could be determined in whole coal, a series of 25 coals were prepared for analysis. For each coal, a low temperature ash, a high temperature ash and the whole coal itself were prepared for X-ray fluorescence analysis sample preparation procedures. When all values were converted to the whole coal basis, the agreement among the three types of coal materials was excellent (Table 2) indicating that the simpler and more rapid whole coal technique is acceptable for the determination of major and minor elements.

#### Determination of Trace Elements in Whole Coal

Trace element determinations on whole coal have been severely handicapped by the lack of analyzed standards. Because of this it has been necessary to prepare calibration curves from samples analyzed in our laboratories by other independent methods. The accuracy of the X-ray fluorescence method is, therefore, limited by the accuracy of the methods used for obtaining the trace element concentrations that were employed in preparing the calibrations. The difficulties encountered in uniformly adding known quantities of trace elements to ground whole coal prohibited the preparation of calibrations in that fashion.

The "light" coal matrix of carbon, hydrogen and oxygen and the relatively small variation of "heavier" trace elements permits their determination with a minimum of interferences. Using the same whole coal procedures as previously described for the determination of major and minor elements, P, V, Cr, Mn, Co, Ni, Cu, Zn, As, Br, Mo, and Pb have been determined directly in 50 whole coals.

The relative errors for all\* elements determined are given in Table 4. These data indicate the precision obtained for the X-ray fluorescence analysis on duplicates of 15 samples of whole coal ground to -325 mesh. Accuracy of the X-ray fluorescence method was evaluated by calculating, from the 50 whole coals analyzed, the mean variation of each element\* from its mean concentration as determined by the other independent methods previously mentioned (Table 5). Detection limits (three standard deviations above background) for each element are also given in Table 5.

#### X-Ray Matrix Corrections for Analysis of Whole Coal

Due to the lack of standards, variations in analyses made by other methods, and errors caused by coal sampling problems; it has been difficult to evaluate the need for X-ray matrix corrections and to select the best method for applying them. However, corrections were necessary because some elements in whole coal such as Fe, Si, and S may vary considerably. For these elements, corrections were applied indiscriminately to all samples because it was impossible to determine the point at which matrix variations required a correction greater than the accuracy limits of the method. We elected to use the minimum number of corrections compatible with reasonably accurate results. As a result the elements Mg, Al, Si, P, S, Cl, K, and Mo were left uncorrected. While these determinations probably could be improved (Berman and Ergun, 1968) they were shown to be adequate for our purposes (Table 2). The Ti and V values were corrected by using the variations in whole coal iron content.

The method of correcting the other elements for matrix variations was that of Sweatman, Norrish and Durie (1963). A total mass absorption was determined by measuring the attenuation of the radiation in question by a thin layer of the sample to be analyzed. The mass absorption coefficient  $M$  was calculated by 
$$M = \frac{A}{W} \ln \frac{C_s}{C_x}$$

where  $A$  = area of sample ( $\text{cm}^2$ );  $W$  = weight of sample in grams;  $C_s$  = intensity in counts per second of the standard; and  $C_x$  = intensity in counts per second of the standard attenuated by the coal sample. Using these coefficients, a corrected value was obtained for the elements determined even when matrix variations were considerable. It should be noted that great care was taken to press the coals to a uniform thickness so that the mass absorption coefficient was affected only by density (for which compensation was made) and matrix considerations.

\* For completeness, whole coal minor element data are also included in the trace element tables.

### Effect of Coal Particle Size Upon Trace Element Analytical Precision

Our results indicated that coals ground to -60 mesh did not yield a consistently acceptable precision for most trace element determinations. Therefore, it was necessary to evaluate the errors associated with the determination of trace elements in coals ground to different particle sizes.

Nine coals, representing a range of trace element concentrations, were carefully ground to pass screens of various mesh sizes (Table 6). Duplicate two gram coal samples for each mesh size were weighed and, then, all were further reduced in size by grinding for 3 minutes in a No. 6 Wig-L-Bug. The final grinding of analysis samples eliminated, as nearly as possible, any variation in the pressed coal discs, which were subsequently prepared for analysis according to Ruch, Gluskoter, and Shimp (1973). In all, over 1000 individual determinations were made in this study.

Table 6 gives the combined means of the differences between duplicate trace element determinations for each coal particle size analyzed. Both the means of the absolute differences (ppm) and the means of the relative differences (absolute difference expressed as a percentage of the concentration) are given. The results show that there is a progressive improvement in precision with decreasing coal particle size.

The ranges of relative differences between duplicate analyses for a number of trace elements at three coal mesh sizes are given in Table 3. With the exception of Br, the ranges are narrower for the -200 and -325 mesh sizes than they are for the -60 mesh coal.

Progressive reduction in coal particle size from -60 to -400 mesh resulted in the improvement of precision for all elements except Br. The combined mean for all elements was reduced below 5% for coal ground to pass a -200 mesh sieve.

These data indicate that for most purposes acceptable precision can be obtained on -200 mesh coal. Further improvement is achieved on grinding to -325 mesh, but this will usually be unnecessary except for analyses to be used as standard values or other special purposes. Variations in the original field sampling of coal would probably negate any improvements in precision that might be gained from grinding below the -325 mesh size.

While this study applied directly to X-ray fluorescence analysis of whole coal, it is felt that it should also apply to any method in which a limited sample (~ 3 grams or less) is taken for analysis.

### Discussion and Conclusions

Good agreement of whole coal results, as determined by X-ray fluorescence, was obtained with those values determined by several other independent methods (Table 5). Some variations among the methods were found to occur at the higher trace element concentrations, especially for the more coarsely ground coals. Because this was true not only of the X-ray fluorescence method, but also of the other methods investigated, it was felt that the variations were due to sampling errors caused by the occurrence of discrete mineral particles such as pyrite and sphalerite in whole coal. This has now been demonstrated to be true by geologists at the Illinois State Geological Survey using the scanning electron microscope.

It is apparent from Table 5 that trace elements determined by the X-ray fluorescence method described in this report are limited to those elements occurring in whole coals at concentrations of a few parts per million or greater. Elements such as Se, Hg, and Sb, which are usually present in whole coal at levels below one ppm, are not capable of being determined by this method.

Our results indicate that X-ray fluorescence provides a highly useful tool for rapid and reasonably accurate analysis of whole coal for trace elements. Because of the speed and simplicity of the method, it is highly adaptable to large scale surveys of coal resources. While the limitations of this simple procedure may preclude the determination of certain elements, the time-saving factor over other methods (40 or 50 to 1 in the case of Br by neutron activation) without loss of accuracy may well make X-ray fluorescence the method of choice for many elements. The availability of improved equipment, such as nondispersive systems and automation, could extend the application of X-ray analysis to a dominant position for the determination of trace elements in whole coal.

TABLE 1 - SPECTROMETER PARAMETERS

Element	X-Ray	2 $\theta$ Angle	Background 2 $\theta$	Crystal	X-Ray Tube	PHA Volts	
						Base	Window
Si	KL <sub>3</sub> & KL <sub>2</sub>	108.01 <sup>o</sup>	111.01 <sup>o</sup>	EDDT	Cr	7	17
Al	KL <sub>3</sub> & KL <sub>2</sub>	142.42	145.95	EDDT	Cr	5	17
Ti	KL <sub>3</sub> & KL <sub>2</sub>	86.12	89.12	LiF	Cr	5	18
Fe	KL <sub>3</sub> & KL <sub>2</sub>	57.51	60.51	LiF	Cr	5	25
Ca	KL <sub>3</sub>	44.85	47.95	EDDT	Cr	14	30
K	KL <sub>3</sub> & KL <sub>2</sub>	50.32	53.90	EDDT	Cr	14	21
Mg	KL <sub>23</sub>	136.69	139.69	ADP	Cr	4	8
V	KL <sub>3</sub> & KL <sub>2</sub>	76.93	80.93	LiF	Cr	5	16
S	KL <sub>3</sub> & KL <sub>2</sub>	75.24	78.38	EDDT	Cr	12	18
Cl	KL <sub>3</sub>	64.94	67.94	EDDT	Cr	11	19
P	KL <sub>3</sub> & KL <sub>2</sub>	110.99	113.99	Ge	Cr	9	15
Ni	KL <sub>3</sub> & KL <sub>2</sub>	48.66	50.36	LiF	Cr	10	27
Cu	KL <sub>3</sub> & KL <sub>2</sub>	45.02	49.67	LiF	Cr	11	28
Zn	KL <sub>3</sub> & KL <sub>2</sub>	41.79	44.25	LiF	Cr	10	22
Pb	L <sub>3</sub> N <sub>5</sub> & L <sub>2</sub> M <sub>4</sub>	28.24	31.24	LiF	Cr	22	28
Br	KL <sub>3</sub> & KL <sub>2</sub>	29.97	35.12	LiF	Cr	25	23
As	KL <sub>3</sub> & KL <sub>2</sub>	34.00	37.00	LiF	Cr	24	23
Co	KL <sub>3</sub> & KL <sub>2</sub>	52.79	53.79	LiF	W	13	16
Mn	KL <sub>3</sub> & KL <sub>2</sub>	62.97	63.97	LiF	W	8	12
Mo	KL <sub>3</sub> & KL <sub>2</sub>	20.33	19.83	LiF	W	36	40
			20.83				
Cr	KL <sub>3</sub> & KL <sub>2</sub>	69.35	68.35	LiF	W	7	15

TABLE 2 - MEAN ABSOLUTE VARIATION  
BETWEEN RAW COAL AND ASH

Element	(%) Average Difference	(%) Maximum Difference
Si	.10	.24
Al	.08	.12
Ti	.012	.030
Fe	.10	.17
Ca	.04	.12
K	.02	.04
P	.002	.005
Mg	.010	.015

TABLE 3 - RANGE OF RELATIVE ERRORS IN  
PERCENT AT THREE WHOLE COAL  
PARTICLE SIZES

Element	-60 Mesh	-200 Mesh	-325 Mesh
V	0.0 - 10.0	.3 - 5.0	.3 - 4.0
P	2.0 - 18.0	2.0 - 10.0	1.5 - 7.5
Ni	1.5 - 25.0	.0 - 20.0	1.5 - 8.0
Cu	.8 - 20.0	.2 - 1.0	.2 - 1.0
Zn	1.2 - 25.0	1.2 - 12.0	.1 - 6.5
Pb	.4 - 23.0	1.2 - 9.5	.4 - 5.0
As	.1 - 6.0	.1 - 4.0	0.0 - 1.5
Br	0.0 - 4.0	0.0 - 3.5	0.0 - 3.0

TABLE 4 - DEVIATIONS ON -325 M  
WHOLE COAL

<u>Element</u>	<u>Standard Deviation</u>	<u>Relative Deviation (%)</u>
	<u>per cent</u>	
Al	.021794	1.77
Si	.05319	1.96
S	.013038	.532
Cl	.0035496	1.13
K	.00370135	2.26
Ca	.005291	1.65
Mg	.002097	3.88
Fe	.021977	1.26
	<u>ppm</u>	
Ti	4.1580	.564
V	1.5801	3.84
Ni	1.11744	4.29
Cu	.74833	3.92
Zn	3.6105	1.37
As	.94291	2.49
Pb	1.5286	2.29
Br	.39047	2.11
P	3.4066	10.92
Co	.4300	4.79
Mn	4.1429	7.53
Cr	1.1402	4.35
Mo	3.1080	23.9

TABLE 5 - COMPARATIVE ACCURACY FOR WHOLE COAL  
AND LIMITS OF DETECTION

<u>Element</u>	<u>Accuracy</u>	<u>Limit of Detection</u>
	<u>per cent</u>	<u>per cent</u>
Al	± .08	.012
Si	± .10	.016
S	± .04	.003
Cl	± .01	.0015
K	± .02	.003
Ca	± .04	.0005
Mg	± .010	.015
Fe	± .10	.005
	<u>ppm</u>	
Zi	± 6.3	7.5 ppm
V	± 3.1	2.5 ppm
Ni	± 1.9	3.5 ppm
Cu	± 2.5	1 ppm
Zn	± 23.	2 ppm
As	± 4.3	3.2 ppm
Pb	± 7.7	1.8
Br	± 1.0	.5
P	± 15.	15 ppm
Co	± 1.3	2.5
Mn	± 3.4	4.5
Cr	± 2.1	1.5 ppm
Mo	± 5.2	5 ppm

TABLE 6 - MEAN ERROR FOR ALL ELEMENTS AT  
VARIOUS COAL PARTICLE SIZES

<u>Mesh size</u>	<u>ppm</u>	<u>(%) Error of Mean Element Concentration</u>
-60 M	± 3.05	8.47
-100 M	± 2.11	6.38
-200 M	± 1.26	4.28
-325 M	± 1.12	2.62
-400 M	± 1.02	1.56
<<400 M	± .93	1.40

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## TRACE IMPURITIES IN FUELS BY ISOTOPE DILUTION MASS SPECTROMETRY

J. A. Carter, R. L. Walker and J. R. Sites

Oak Ridge National Laboratory\*  
Post Office Box Y  
Oak Ridge, Tennessee 37830

## INTRODUCTION

Elements considered toxic to living organisms are present from the low ppb to the high ppm concentration range in coal and other fuels used as energy sources. With over half of the consumption of coal being used by large central power stations, the concentrated quantities of such potentially harmful elements as Hg, Cd, Pb, U and others are appreciable. In the USA, for example, with an average annual coal consumption of over 500 million tons, any element present in coal at the 1 ppm level generates a waste problem of 500 tons. Many of the elements of interest are concentrated in the particulate fly ash or in the bottom slag. The use of efficient electrostatic precipitators, however, prevent most of the fly ash from being dispersed into the atmosphere. The fly ash and the bottom slag then become a storage and containment problem.

The major thrust of this research effort has been to demonstrate the capabilities of spark source and thermal emission mass spectrometry for determining the fate of trace elements in coal fired central power plants. Additionally, isotope dilution methods for the analyses of Pb, Cd and Hg in gasolines and other petroleum fuels have been developed and used for referee and evaluation purposes.

## EXPERIMENTAL

## Spark Source Mass Spectrometry

The spark source mass spectrometer (SSMS) in this research was a commercial Mattauch-Herzog double focusing instrument; a schematic representation is shown in Fig. 1. In a SSMS analysis, an ion beam of the substance being investigated is produced in a vacuum by igniting a spark between two conductors employing a pulsed high-frequency potential of 50 kV. During this process, the electrode substance is evaporated and ionized. The produced ions are accelerated through the source slits by a constant potential of 25 kV into an electrostatic radial field which functions as an energy filter. As the ions pass through the magnetic field, deflection occurs so that a splitting of the ion beam takes place according to the mass-to-charge ratio; these charged particles impinge in focus on an ion-detector (photographic plate or photo multiplier) to form the mass spectrum. From the position of the lines and the relative intensity, elemental identification and abundance measurements can be made when the total ion beam current is known; this total ion current is measured by a monitor located just ahead of the magnetic analyzer. The resolution of the AEI-702R instrument used was greater than 3000. Ilford Q-2 photographic emulsions were used to record the mass spectra.

\*Operated for the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

Conducting electrodes for general scan analyses were prepared by mixing the pulverized coal or fly ash with an equal amount of pure Ag powder (99.999% Ag). The homogenized mixture was then pressed in polyethylene slugs in an isostatic electrode die at 25,000 psi for 1 min. The nominal electrode size was 1 cm x 0.15 cm. Sets of graded exposures were made from these electrodes so that the concentration range from 0.03 ppm up to the percent range was covered. Photoplates were interpreted according to the techniques given by Kennicott.<sup>(1)</sup> In fly ash and coal samples, Fe was determined chemically so the isotopes of Fe could be used as an internal standard.<sup>(2)</sup> Computerized sensitivity values were used.

#### Isotope Dilution By Spark Source Mass Spectrometry

A unique and quite different approach to the determination of trace elements in solids, liquids and gases involves the use of the isotope dilution technique. This method has been operational for some time with mass spectrometers, using thermal ionization sources for solids and electron bombardment sources for gases, giving accurate results with small samples; however, not until recently has it been used for analyzing environmental samples with spark source mass spectrometers.<sup>(3)</sup> The general method of isotope dilution has been described by Hintenberger.<sup>(4)</sup> For each element to be determined, an enriched isotope, usually of minor abundance, is mixed with the sample. The isotopic ratios, altered by spike additions, are then measured on a portion of the sample by mass spectrometry. Even though the method is limited to elements having two or more naturally occurring or long-lived isotopes, it possesses the great advantage over other analytical techniques of being very sensitive and accurate, and relatively free from interference effects. Thermal source and electron bombardment mass spectrometers are well suited for isotope dilution, but they display very different sensitivities for various elements; whereas spark source mass spectrometers have similar sensitivities for all elements and can therefore be used without deleterious effects from a complete matrix change.

Fig. 2 shows a mass spectrum of cadmium spiked with enriched  $^{106}\text{Cd}$ . The solid line at position 106 represents the  $^{106}\text{Cd}$  spike and the dashed lines represent the relative abundances for the other Cd isotopes. The dashed line at juxtaposition at 106 is the relative abundances of  $^{106}\text{Cd}$  as it occurs in nature. Table I shows the IBM 1130 computer programmed output for a typical isotope dilution analysis. The program is flexible in that the spike size, sample size, spike composition, and percent transmittance can all be variables. The three sets of data under 106 and 114 are percent transmittance for three photoplate exposures taken, and the results are reported in nanograms per gram.

#### Isotope Dilution By Thermal Emission Mass Spectrometry

For the quantitative measurement of Pb and U in coal and fly ash and Pb in gasoline, a three-stage thermal emission mass spectrometer (TEMS) was used (Fig. 3). The basic design of the instrument is based on that developed by White and Collins 1954<sup>(5)</sup> and modified at ORNL. The addition of an electrostatic third stage increased the abundance sensitivity to  $10^8$  as described by Smith et al.<sup>(6)</sup>

The two magnetic stages are 30-cm radius followed by an electrostatic analyzer with a radius of 43.25 cm. The vacuum system is of all-metal construction

and is bakeable to 300°C. The analyzer region of the instrument is pumped with ion pumps and is maintained at a pressure of  $10^{-5}$  torr. A combination titanium sublimation-ion pump is used to obtain operating pressures in the source region in the  $10^{-5}$  torr range. A Nier thick-lens source,<sup>(7)</sup> used in conjunction with a sample wheel arrangement,<sup>(8)</sup> makes it possible to analyze as many as ten samples per day.

Ions are detected by a secondary electron multiplier behind the receiver slit. The pulses from the multiplier are accumulated in a 400-channel analyzer used in the time base mode. This arrangement allows the maximum sensitivity with respect to sample size. Mass measurements are made by sweeping the accelerating voltage across the region of interest, 233 through 238 for U; 204 through 208 for Pb. The determinations of uranium and lead in coal and fly ash and Pb in gasoline, both quantitatively and isotopically, are done by isotope dilution with enriched spikes of  $^{235}\text{U}$  and  $^{204}\text{Pb}$ .

Pb Analysis by TEMS. Lead analyses are made utilizing the gel technique described by Cameron et al. 1969.<sup>(9)</sup> Lead ions are thermally produced at rhenium filament temperatures ranging between 1100-1300°C depending somewhat on the sample size. A loading of 10 nanograms provides enough sample to allow an analysis consisting of 10 runs of 200 sweeps across the masses of interest.

U Analysis by TEMS. Uranium ions are thermally produced at rhenium filament temperatures ranging from 1700-1850°C. Small quantities (10-100 nanograms) of uranium in the form of  $\text{UO}_2(\text{NO}_3)_2$  produce sufficient ions for a precise analysis. A benzene reduction procedure has been developed at ORNL which produces only metal ion signals. This procedure produces a very clean uranium spectrum and increases the sensitivity of the measurement. As in the analysis of lead, an analysis consists of at least 200 sweeps across the masses of interest.

Preparation of Coal and Fly Ash for Isotope Dilution Analysis. Separate aliquots of coal and fly ash are weighed out and spiked with  $^{204}\text{Pb}$  and  $^{235}\text{U}$ , respectively. The chemical treatment and extraction of Pb and U from coal and fly ash are identical except coal is ashed at 450°C before chemical treatment. The samples are dissolved with a mixture of  $\text{HF}\cdot\text{HNO}_3\cdot\text{HClO}_4$  in Teflon beakers. The lead is separated by dithizone extraction, evaporated to dryness, redissolved in dilute  $\text{HNO}_3$  and 10 ng loaded on filaments with silica gel for mass analysis.

The uranium is separated after dissolving the sample as described for lead by extraction with TBP from 4 M  $\text{HNO}_3$ . After the organic phase is scrubbed with 4 M  $\text{HNO}_3$ , the uranium is back extracted into distilled water and evaporated to dryness. The uranium is loaded on a rhenium filament by dissolving the purified sample in a small volume of 0.05 M  $\text{HNO}_3$  for analysis.

Preparation of Gasoline for Isotope Dilution Analysis. Aliquots of gasoline are spiked with  $^{204}\text{Pb}$  and treated by either a wet chemical method or the bromine oxidation method described by Griffing and Rozek.<sup>(10)</sup>

The wet chemical procedure consisted of refluxing first with  $\text{HNO}_3$  until the initial reaction subsided, then  $\text{HClO}_4$  was added to the flask and the reflux continued until the reaction was complete. The resulting solution containing the inorganic lead was finally evaporated to near dryness, diluted to a suitable Pb concentration with dilute  $\text{HNO}_3$  and loaded onto Re filaments for M.S.

In the bromine method,  $\text{Br}_2$  in  $\text{CCl}_4$  was added to the gasolines in a test tube. Complete conversion to lead bromide was assured by heating. The resulting lead bromide precipitate was dissolved with dilute  $\sim 1 \text{ M}$   $\text{HNO}_3$ . The mixture was centrifuged and the organic layer discarded; the aqueous solution was adjusted for M.S. analyses. Either of the procedures works satisfactorily, but the  $\text{Br}_2$  method is much easier, faster and has less possibility for contamination.

#### RESULTS AND DISCUSSION

The bulk of the samples for this study came from TVA's Allen Steam Plant at Memphis, Tennessee. The sampling points (Fig. 4) included inlet air, coal, bottom ash, precipitator inlet and outlet at the 268-ft. stack level. During the two-week sampling period the unit was operated under steady state conditions at 240 MW<sup>(11)</sup> with a uniform coal supply so that a mass balance might be established for a number of elements. All the coal from southern Illinois was washed and crushed by TVA so that 90% was <4 mesh. Nominal coal analysis indicated the following composition: 9.5% moisture, 34% volatiles, 43% fixed carbon, 13% ash and 3.4% sulfur.

The isotope dilution results in Table II are on fuel source samples considered homogeneous; these samples were obtained from NBS. The results in Table III are from the sampling points as indicated in Fig. 4. These summarized results are mostly by the SSMS general scan technique; the general scan technique has an estimated accuracy of better than  $\pm 50$  percent, while the isotope dilution measurements are limited by the emulsion detector to  $\pm 3$ -5%. The results are in terms of grams of metal flow per minute. The mass balance for the various elements was computed by the following equations:

$$Q_c(m) = C_c(m) \times (\text{g coal/min}) \quad (1)$$

$$Q_{pi}(m) = C_{pi}(m) \times (\text{g fly ash/min}) \quad (2)$$

$$Q_{ba}(m) = C_{ba}(m) \times (\text{g ash in coal} - \text{g fly ash/min}) \quad (3)$$

$$\text{Imbalance, \%} = \frac{(Q_{pi} + Q_{ba} - Q_c)}{Q_c} 100 \quad (4)$$

where  $Q_c(m)$ ,  $Q_{pi}(m)$  &  $Q_{ba}(m)$  are flow rates of metal (m) in  $\text{g min}^{-1}$  for coal, precipitator inlet and bottom ash, respectively, and  $C(m)$  is concentration in weight fraction. Coal consumption during the sampling was at a rate of  $82.5 \text{ tons hr}^{-1}$ , or  $1.25 \times 10^6 \text{ g min}^{-1}$ , and the fly ash flow rate was measured at  $4.9 \times 10^4 \text{ g min}^{-1}$ .

The metal balance for all the elements analyzed by mass spectrometry is good, but on the average shows a negative imbalance of 20%. Metals showing high imbalance, i.e., Hg, As and Se probably were in the gaseous state at the sample points. An example of this was the case for Hg in which a precipitator outlet sample showed a flow of  $0.02 \text{ g min}^{-1}$ , and at a point of this sampling the particulates are much cooler than the fly ash at the precipitator inlet.

The average imbalance for the elements measured by isotope dilution mass spectrometry with lower volatility showed an imbalance range from -8% to +12%; these results indicate the usefulness of mass spectrometry in evaluating environmental impacts.

#### ACKNOWLEDGMENTS

The authors gratefully acknowledge the assistance and cooperation of the many personnel of the Tennessee Valley Authority. This work was supported by the National Science Foundation Interagency Agreement No. AEC 40-237-70 and NSF AG 398. The work was carried out at ORNL which is operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

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Table I

Sample Computer Output for Cadmium by Isotope  
Dilution Spark-Source Mass Spectrometry

CD	106	114	VOL	CONCK
SPIKE	88.400	2.500	1.000	1.000
SAMPLE	1.220	28.900	1.000	

	SAMPLE	NANO-GM	106	114
5	SOIL 318R	4005.000	19.3	16.2
5	SOIL 318R	4032.000	46.9	41.3
5	SOIL 318R	3933.000	64.6	60.0

Table II

## ISOTOPE DILUTION RESULTS

Sample Type	Concentration, wt ppm			
	U TEMS	Pb TEMS	Pb SSMS	Cd SSMS
Coal	1.22		28	0.28
	1.18		26	0.34
	1.22		28	0.32
	1.22		30	0.32
Fly Ash	11.9		79	1.8
	11.7		78	2.2
	11.6		79	1.9
	11.6		76	1.5
Gasoline (a)		285 (b)	284 (c)	<.01
		282	284	<.01
		284	285	-
		283	279	-
Fuel Oil (a)			0.27	0.022
			0.28	0.021
			0.26	0.018
			0.23	-

(a) Results in  $\mu\text{g/ml}$ ;

(b) Wet oxidation;

(c)  $\text{Br}_2$  oxidation with TEMS.

Table III

IMPURITY MASS FLOW IN A STEAM PLANT  
(Flow rate in  $\text{g min}^{-1}$ )

Element	Coal	Bottom Ash	Precipitator Inlet	Imbalance %
Al	13,000	5,500	7,300	- 1.5
Ca	6,000	3,300	1,500	-20
Fe	25,000	10,000	4,900	-40
K	700	550	340	+27
Mg	1,800	770	340	-38
Na	370	220	150	0.0
Ti	880	220	240	-48
Mn	130	110	34	+11
As	6.2	0.22	2	-64
Be	<5	<1.1	0.83	--
Cd <sup>a</sup>	0.63	0.30	0.28	- 7.9
Cu	63	22	19	-35
Pb <sup>a</sup>	9.3	0.45	10	+12
Ni	<100	55	24	-21
Sb		0.8	0.5	--
Se	7.5	2.2	1	-58
V	37	11	17	-24
Zn <sup>a</sup>	110	2.0	100	- 7.3
Hg <sup>a</sup>	0.08 <sup>b</sup>	0.007 <sup>b</sup>	0.007	*

<sup>a</sup> Isotope dilution; <sup>b</sup> Atomic absorption; <sup>c</sup> Ppt outlet 0.02.

\*Most Hg flow is in stack gas.

## FIGURE CAPTIONS

Figure 1. Schematic diagram of a double focusing spark-source mass spectrometer.

Figure 2. Computer plot of a cadmium spectrum spiked with enriched  $^{106}\text{Cd}$ .

Figure 3. Schematic diagram of the three-stage mass spectrometer.

Figure 4. Schematic diagram of a TVA coal-fired steam plant.

ORNL-DWG. 73-3117

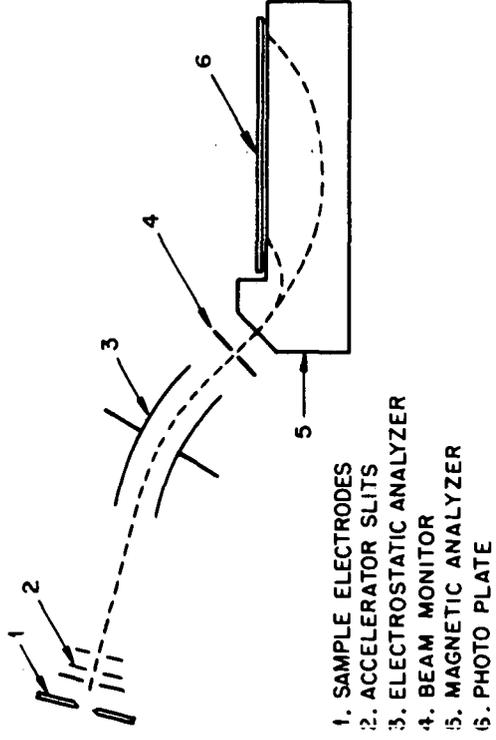
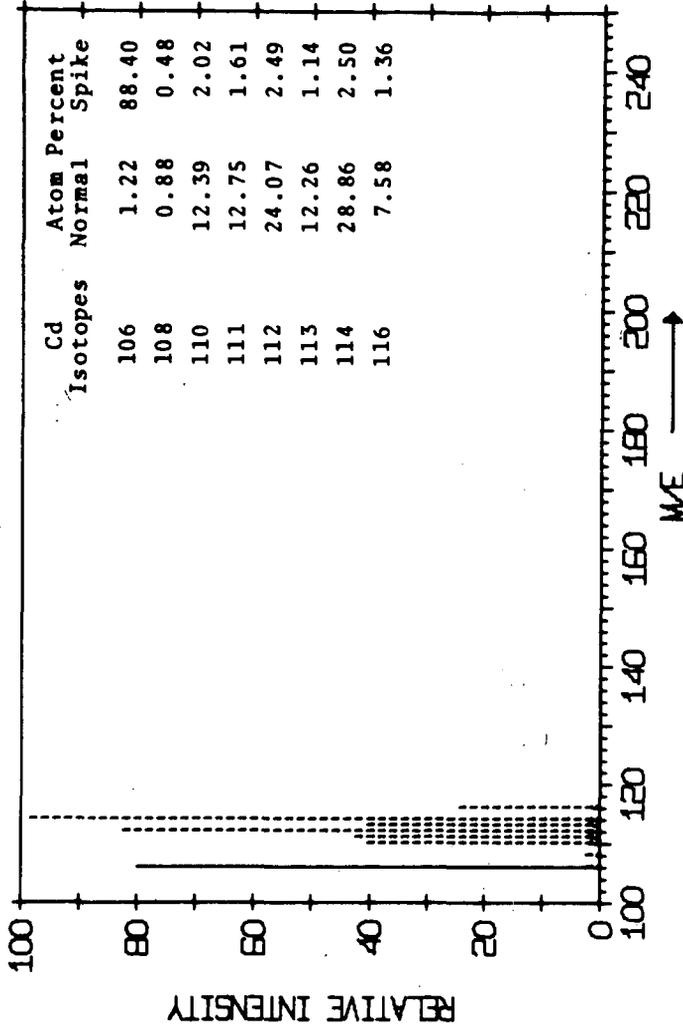


Figure 1. Schematic Diagram of a Double Focusing Spark-Source Mass Spectrometer

ORNL-DWG. 73-3116

Figure 2. Computer Plot of a Cadmium Spectrum Spiked with Enriched <sup>106</sup>Cd

ORNL-DWG. 70-9157

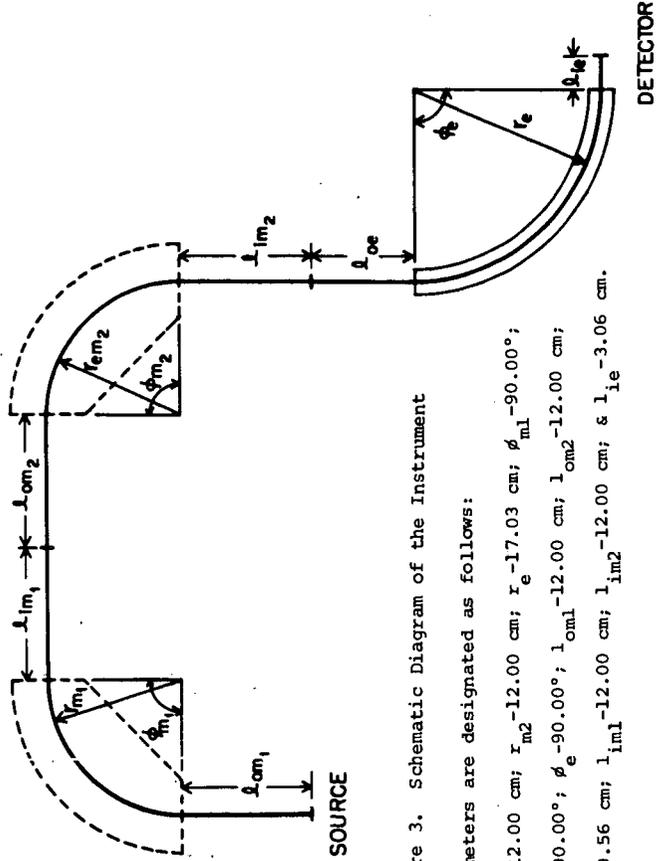


Figure 3. Schematic Diagram of the Instrument

Parameters are designated as follows:

- $r_{m1}$ -12.00 cm;  $r_{m2}$ -12.00 cm;  $r_e$ -17.03 cm;  $\phi_{m1}$ -90.00°;  
 $\phi_{m2}$ -90.00°;  $\phi_e$ -90.00°;  $l_{om1}$ -12.00 cm;  $l_{om2}$ -12.00 cm;  
 $l_{oe}$ -9.56 cm;  $l_{im1}$ -12.00 cm;  $l_{im2}$ -12.00 cm;  $s$   $l_{ie}$ -3.06 cm.

ORNL - DWG. 73 - 3118

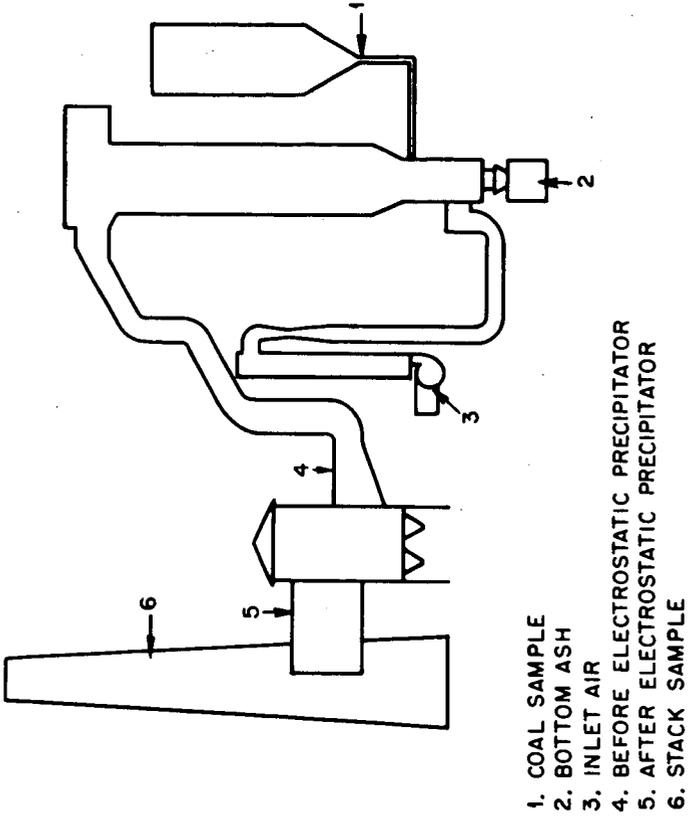


Figure 4. Schematic Diagram of a TVA Coal-Fired Steam Plant

## TRACE IMPURITIES IN COAL

E. N. Pollock

### Introduction

As trace impurities in the environment become of increasing concern, those materials that can have important impact on the environment are coming under careful scrutiny. Coal, along with the other sources of energy, is a material of major interest. The Federal Environmental Protection Agency is developing a growing list of environmental contaminants that will have to be monitored in the energy sources. These include mercury, beryllium and asbestos presently, but other elements that have undesirable physiological effects on plant and animal life such as cadmium, arsenic, lead and fluorine will receive increasing attention.

The determination of potentially toxic elements in coal has received little effort in the past. In many cases early information was unreliable because of poor methodology. Coal is a complex material containing both organic and inorganic phases and analyses in the past have suffered from both losses and contaminations in dissolution. Beyond the elemental analysis, the determination of elemental form, whether inorganic or organically bound, will condition the environmental impact. The investigators in the determination of mercury in coal have experienced all these problems in attempting to follow the mass balance of mercury in the combustion of coal.

This paper is still only concerned with elemental analyses. However, methods were investigated for most elements that could be potential environmental pollutants.

Two different general analytical techniques were employed: mass spectrometry and wet chemical methods. Six elements were determined by mass spectrometry and seventeen elements were determined by a variety of wet chemical methods.

### Trace Elements by Spark Source Mass Spectrometry

The spark source mass spectrometric (SSMS) technique is one of the most sensitive instrumental methods for determining inorganic impurities in a variety of materials.<sup>1</sup> Since the advent of electrical detection, this method has become much more rapid and reliable<sup>2</sup>. A method has been developed for the determination of six elements of toxicological interest and correlation between these impurities in the original coal and the coal ash will be shown. Since no primary standards are available at this time for coal, all mass spectrometric data is compared to atomic absorption spectrophotometry (AAS) values determined on the same samples. Relative standard deviations are on the order of 6 to 15% for the mass spectrometric data and 2 to 3% for the atomic absorption values.

#### Experimental

An AEI MS-7 spark source mass spectrometer equipped with electrical detection was used in this study. A description of this apparatus complete with manufacturer's accessories and modifications has been described previously and will not be detailed here<sup>2</sup>. The instrument was used in the peak-switching mode only to provide more precise analyses. The instrument operating parameters are given in Table I. The integrated multiplier current for each preset position on the peak switches (each position corresponding to a different isotope to be determined) was displayed on a digital voltmeter. These intensity values were then used to calculate the actual concentration.

#### Standard and Sample Preparation

Since no primary standards were available at the time of this investigation, AAS was used to provide analyses on several different coals so that they could be used as secondary standards. Representative portions of

each sample and standard were obtained by grinding and splitting. The samples thus obtained (< 100 mesh) were then weighed into porcelain crucibles and placed into a vented cold furnace and the temperature is elevated to 300°C in one-half hour. The temperature was then raised to 550°C for one-half hour and then to 850°C for an additional hour. The crucibles were then removed from the furnace and the ash dry mixed with a glass stirring rod. The crucibles were then returned to the furnace at 850°C without venting until ashing was completed (usually one additional hour). Samples for SSMS were reground with a boron carbide mortar and pestle and diluted with two parts of high purity graphite. The samples with graphite were placed in polystyrene vials with two or three 1/8" diameter polystyrene beads and mixed in a spex mill for twenty minutes. Electrodes were prepared from the powders using the AEI briquetting die and polyethylene slugs.

Once the electrodes had been prepared, they were placed in the source of the instrument using a standardized mounting procedure. Repetitive exposures were then recorded for each element of interest in the standards and unknowns. The concentrations were calculated from the following relationship:

$$\frac{C_x}{C_s} = \frac{I_x}{I_s}$$

where  $C_s$  and  $C_x$  are the concentrations, the subscripts s and x refer to the standard and unknown, respectively:

$I_s$  and  $I_x$  are the intensities (integrated multiplier currents).

### Results and Discussions

One of the questions posed by the dry ashing of coal is whether or not some of the elements may be lost through volatilization during the combustion process. A comparison of wet ashing and dry ashing of some of the elements analyzed in this study is given in Table II. This data is based

solely on atomic absorption analyses. As can be seen from the table, the agreement between the two sets of data is generally very good. This would seem to indicate that none of these particular elements are lost during the dry ashing of coal. This data does not, however, allow one to make this same generalization for all elements since these are the only elements determined by both ashing techniques during this investigation. Kometani, et. al.<sup>3</sup> have indicated that the presence of sulfates prevents the loss of many elements during dry ashing; and since coal contains appreciable amounts of sulfates, this may help to explain the agreement between the two methods of ashing. Vapor pressure data also imply that these metals could possibly be present as oxides or silicates. Since ash contents of the coals studied varied from 5 to 25% according to the geographical location, the standards for the SSMS analysis were chosen so as to coincide with the approximate area from which the actual samples were taken. Table III is a comparison of the AAS and SSMS data obtained on ten different coal samples from three or four different geographical areas. These values are based upon the metal concentration in the whole coal whereas the analysis was performed on the ash. Again, there is generally very good agreement between the two different methods used. This data also shows that hydrocarbon interference is not a problem at these concentration levels. A very volatile element such as mercury could not be analyzed using this method as it has been postulated that it is pumped away during heating caused by the excitation process, depending upon the parameters selected. The validity of SSMS with electrical detection has proven to be an acceptable method of analysis. Another important aspect of this study was the time involved per sample. Sample and standard preparation (including ashing), electrode preparation, instrument preparation (setting peaks), running of ten samples and four standards, data reduction and conversion to concentration in the whole coal required only fifteen hours. This represents 84 separate analyses. This fifteen

hours also includes sample turn-around time and five separate 0.3nC monitor exposures for each element in each sample and standard. The precision data for the SSMS technique is 6 to 15% relative. The detection limits for the elements studied are on the order of 1 to 2 ppmw in the whole coal using the previously mentioned parameters. This is not necessarily the lower limits as such items as exposure (nC), multiplier gain and sample dilution may increase or decrease this level. From the intensity values obtained during this investigation, absolute detection limits ranging between 0.1 and 0.3 ppm by weight with whole coal would be a realistic estimate. These lower values were not actually determined. The average deviation from the AAS results is 29.2%.

#### Trace Elements by Wet Chemical Methods

The determination of trace impurities by wet chemical methods can immediately be separated into two major divisions. First, those elements that can be dry ashed, leached in acid and the analysis completed by conventional AAS. These elements are Li, Be, V, Cr, Mn, Ni, Cu, Zn, Ag, Cd and Pb. Second, those that require specialized techniques.

1. Hg-O<sub>2</sub> bomb combustion followed by flameless AAS.
2. As, Bi and Sb - dry ashing and acid dissolution followed by determination of their hydrides using AAS.<sup>5, 6</sup>
3. Se-combustion and cold trapping<sup>7</sup> followed by determination as its hydride using AAS.
4. F - O<sub>2</sub> bomb combustion<sup>8</sup> followed by specific ion analysis<sup>9</sup>.
5. B - dry ashing followed by Na<sub>2</sub>CO<sub>3</sub> fusion, dissolution in dilute H<sub>2</sub>SO<sub>4</sub>, then followed by colorimetric determination with carminic acid<sup>10</sup>.

#### Determination of Li, Be, V, Cr, Mn, Ni, Co, Cu, Zn, Ag, Cd and Pb

Coal samples are prepared and ashed as described in the procedure employed for SSMS. Five gram samples of coal are used. The ash is placed in 100 ml teflon beaker containing 5 ml of HF (conc.) and 15 ml of  $\text{HNO}_3$  (conc). Warm to dissolve the ash, then evaporate the solution just to dryness. Add water and a few drops of  $\text{HNO}_3$ , then transfer to a 100 ml volumetric flask. Make to volume with water and mix. Immediately transfer to a plastic bottle to preserve as a stock solution for the conventional AAS determinations of Li, Be, V, Cr, Mn, Ni, Co, Cu, Ag, Cd and Pb.

Samples were also prepared for conventional AAS determination by wet ashing approximately 5.0 grams of coal in a mixture of  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ .

#### The Determination of Mercury

A coal sample is decomposed by burning a combustion bomb containing a dilute nitric acid solution under 24 atmospheres of oxygen pressure. After combustion, the bomb washings are diluted to a known volume and mercury is determined by atomic absorption spectrophotometry using a flameless cold vapor technique.

#### Procedure

Transfer approximately 1 gram of 60 mesh X O coal to a clean combustion crucible and weigh to the nearest 0.1 milligram. Transfer 10 ml of 10% nitric acid to the bomb, place the crucible in the electrode support of the bomb, and attach the fuse wire. Assemble the bomb and add oxygen to a pressure of 24 atmospheres (gauge). Place the bomb in the calorimeter (a cold water bath in a large stainless steel beaker is also satisfactory) and ignite the sample using appropriate safety precautions ordinarily employed in bomb calorimetry work.

After combustion, the bomb should be left undisturbed for 10 minutes to allow temperature equilibration and the absorption of soluble vapors. Release the pressure slowly and transfer the contents of the bomb (and crucible) to the mercury reduction vessel by washing with 10% nitric acid. Rinse the bomb, electrodes, and crucible thoroughly with several small washings of 10% nitric acid, then dilute the contents of the reduction vessel with 10% nitric acid to a total volume of 50 ml. Proceed with the determination as described under Standardization. Determine the amount of mercury in micrograms and divide by the sample weight in grams to obtain the mercury value in parts per million.

#### Standardization

Add an aliquot of a standard mercury solution to contain 0.1 micrograms of mercury to the mercury reduction flask. Add  $\text{KMnO}_4$  (3%) dropwise until the pink color persists. Adjust the volume to 100 ml, then add in order 5 ml of  $\text{HNO}_3$  (1:2),  $\text{H}_2\text{SO}_4$  (1:1) and hydroxylamine hydrochloride. When the pink color fades, add 5 ml of the  $\text{SnCl}_2$  (10%) and immediately connect into the system. Start the pump which circulates the mercury in the vapor phase through the optical cell in the atomic absorption spectrophotometer with the mercury lamp optimized at 253.7 nm and normal operating conditions as established by the AA instrument manufacturer. Samples are run by taking all or an aliquot from the  $\text{O}_2$  bomb combustion stock solution.

#### The Determination of Arsenic, Antimony and Bismuth

As, Sb and Bi can be determined by AAS after generation and evolution of their hydrides. The hydrides are formed by the reaction of nascent hydrogen generated by magnesium metal in a  $\text{TiCl}_3\text{-HCl}$  solution. A modified Perkin-Elmer High Sensitivity Arsenic-Selenium Sampling System can be used with any atomic absorption spectrophotometer.

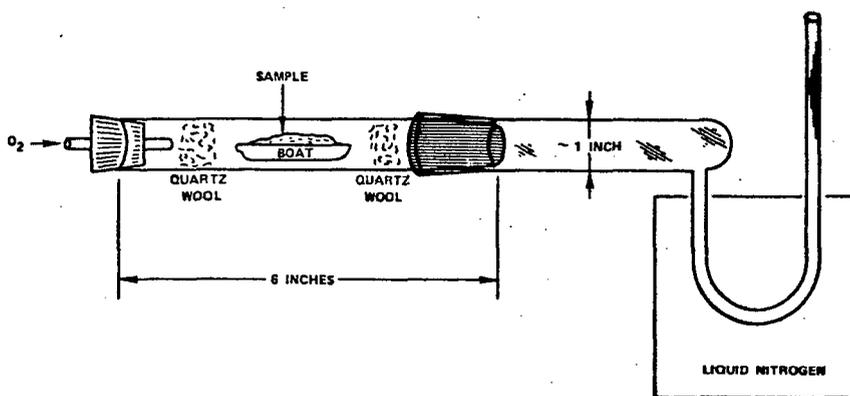
Coal samples for the determination of As, Sb and Bi can be ashed by the method previously described for Li, Be, etc. However, the ash should be leached in HF and HCl. Care must be taken in warming not to lose volatile chlorides. If  $\text{HNO}_3$  is used in place of HCl, a mixed KI and  $\text{SnCl}_2$  must be used in place of  $\text{TiCl}_3$  to generate nascent hydrogen; however, the HCl system is preferred.

A separate aliquot of HCl-HF sample containing up to 0.3 micrograms of As or up to 0.6 micrograms of Sb or Bi is placed in the hydride generation flask. Add 10 ml of  $\text{TiCl}_3$  (1% in HCl) and adjust the volume to 25 ml with water. After flushing the system with argon for fifteen seconds, add a one inch length of 1/8 inch diameter magnesium rod to the flask through the pinch damp. Allow one minute for collection time in the expansion vessel. Then release gases into the argon-hydrogen entrained air flame using a triple slot-type burner and the AAS manufacturer's standard practices. Blank and appropriate standards are run for each of the elements.

#### The Determination of Selenium

The prior separation of selenium from the bulk of the coal sample uses the combustion technique as described by H. L. Rook<sup>7</sup>. It was originally used in a neutron activation analysis. The equipment was modified to use a quartz combustion tube 5 1/2 inches long connected by a ground glass joint to a second section 3 1/2 inches long. The section ends with a U-tube which can be immersed in a Dewar Flask containing liquid  $\text{N}_2$  or some other suitable coolant. For analyses, an 0.5 gram sample is weighed into a porcelain boat and inserted into the combustion tube with an  $\text{O}_2$  flow of  $\sim 30$  cc/min. With the cold trap in place, the sample is ignited by heating the combustion tube with a meker burner. The coal sample is allowed to burn freely, the temperature is then raised to the maximum of the burner for five minutes. The combustion tube is cooled for five minutes and separated from the condenser section. The condenser is removed from the cold trap and allowed to warm to ambient

temperature. Add 10 ml of HCl to the condenser and flush into a 50 ml volumetric flask. Wash condenser with water and add rinsings to the volumetric flask. Make to volume with water and mix. Take an aliquot of 15 ml or less containing up to 0.3 micrograms of Se and proceed as in the method for As, Sb, and Bi by AAS as previously described.



SELENIUM COMBUSTION APPARATUS

#### The Determination of Fluorine

A coal sample is decomposed by ignition in a combustion bomb containing Na<sub>3</sub>CO<sub>3</sub> solution under 24 atmospheres of oxygen pressure. After combustion, the bomb washings are diluted to a known volume and an aliquot is taken to determine F by the standard Orion specific ion procedure.

Transfer approximately 1 gram of coal to a combustion crucible and weigh to nearest 1.0 mg. Transfer 5 ml of Na<sub>2</sub>CO<sub>3</sub> solution (5%) to the bomb, place crucible in the electrode support and attach the fuse wire. Assemble the bomb and add oxygen to a pressure of 24 atmos. Place the bomb in a cold water

bath and ignite the sample using appropriate safety precautions.

After combustion, the bomb should be left undisturbed for ten minutes to allow temperature equilibration and absorption of the soluble vapors. Release the pressure slowly and transfer contents of the bomb (and crucible) into a 25 ml volumetric flask. Make several small washings with water and add rinsings to the volumetric flask. Make to volume with water and reserve the stock solution in a plastic bottle.

Using an expanded scale pH meter, such as the Orion 801, pipet 10 ml of the stock solution into a small beaker and add 10 ml of Tisab (Orion Cat. No. 94-09-09), determine the electrode potential using a fluoride electrode Orion 94-09. Comparison is made by bracketing with fluoride standards prepared similarly.

#### The Determination of Boron

After dry ashing in the manner used in the Li, Be, etc. procedure, the ash is fused with  $\text{Na}_2\text{CO}_3$ , leached in water and acidified with  $\text{H}_2\text{SO}_4$ . The colorimetric carminic acid method<sup>6</sup> is then used for the determination of boron.

Weigh approximately 1 gram of coal into a platinum crucible and carefully ignite in a vented oven. Gradually increase the temperature to  $850^\circ\text{C}$  and maintain for one hour. Remove from oven and add 2 grams of  $\text{Na}_2\text{CO}_3$  and fuse for ten minutes. Leach in 25 ml of warm water in a teflon beaker. When dissolution is complete, add 10 ml of  $\text{H}_2\text{SO}_4$  carefully. Transfer to a 50 ml volumetric flask. Make to volume with water and reserve in a plastic bottle. Place a 5 ml aliquot or less in a 50 ml volumetric flask, make to 5 ml volume with  $\text{H}_2\text{SO}_4$  (3.6M) if less than 5 ml aliquot was used. Aliquot should contain 0 to 100 micrograms of B. Then add 20 ml of chilled  $\text{H}_2\text{SO}_4$  (18M) and swirl. Then add by pipet 20 ml of carminic acid (0.92 grams in  $\text{H}_2\text{SO}_4$  18M). Make to volume with  $\text{H}_2\text{SO}_4$  (18M) and determine absorbance in 1 cm cells in a spectrophotometer at 605 nm with a reagent blank in the reference cell. Compare to a standard curve containing 0 to 100 micrograms.

TABLE I

## Operating Parameters

Spark Variac	35%
Pulse Repetition Rate (pps)	100
Pulse Length ( $\mu$ sec)	100
Source Slit	0.002"
Multiplier Slit	.002"
Moniter Exposure	0.3nC
Multiplier and Amplifier Gains	Variable according to sample elements and concentration
Electrodes Vibrated	

Cu	
ASH	LEACH
1	17 16
2	12 15
3	50 50
4	13 14
5	9 9

Mn	
ASH	LEACH
1	67 64
2	179 169
3	122 128
4	12 15
5	8 7

Ni	
ASH	LEACH
1	19 15
2	4 6
3	84 85
4	13 12
5	7 5

Zn	
ASH	LEACH
1	121 110
2	7 9
3	1420 1450
4	16 23
5	17 19

Cd	
ASH	LEACH
1	2.8 2.8
2	0.6 0.6
3	13.1 12.8
4	0.6 <0.5
5	<0.5 0.5

Pb	
ASH	LEACH
1	13 15
2	8 16
3	105 111
4	13 18
5	8 8

Be	
ASH	LEACH
1	2.2 2.4
2	0.4 0.7
3	2.3 2.6
4	1.6 2.2
5	0.3 0.8

Li	
ASH	LEACH
1	6.8 8.0
2	9.5 11.2
3	17.1 20.8
4	11.8 12.8
5	3.1 3.6

V	
ASH	LEACH
1	55 41
2	10 10
3	43 43
4	18 22
5	7 10

DRY ASHING  
VS  
ACID LEACHING OF COAL

Cu	
MS	AAS
14	17
23	16
22	18
33	29
11	13
32	29
12	24
38	61
13	14
18	18

Zn	
MS	AAS
13	9
41	45
17	12
22	24
41	39
84	12
8	13
660	852
18	20
50	36

As	
MS	AAS
7.7	7.5
3.2	1.5
6.0	4.5
7.7	4.5
2.4	1.0
9.0	4.0
1.8	3.0
3.8	6.5
8.0	5.0
5.6	1.5

Mn	
MS	AAS
33	37
7200	193
90	65
101	93
62	52
124	96
11	19
143	117
22	21
73	49

Ni	
MS	AAS
14	23
23	30
21	31
14	21
14	22
28	28
7	15
41	81
7	22
15	18

Cr	
MS	AAS
26	24
20	12
21	17
12	16
18	19
19	12
13	13
36	31
15	20
37	16

V	
MS	AAS
25	32
21	21
35	23
43	24
24	25
24	21
15	24
20	40
61	37
27	30

TRACE  
ELEMENTS  
IN  
COAL

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"EPA'S NATIONAL FUELS SURVEILLANCE NETWORK" - Robert H. Jungers, Robert E. Lee, Jr. and Darryl J. von Lehmden, Environmental Protection Agency, National Environmental Research Center, Research Triangle Park, North Carolina 27711.

Implementing the Clean Air Act as amended in 1970 may require manufacturers of fuel and fuel additives to register their products with the Environmental Protection Agency. As an integral part of this program, a Fuels Surveillance Network was established in 1972 for the nationwide collection of fuel samples through the EPA regional offices. These samples are submitted to the National Environmental Research Center, Research Triangle Park, North Carolina, for extensive trace element analysis and for major fuel additive component analysis. The analytical data derived from the network samples will be used in a multiplicity of ways. The information will be used to verify manufacturer-registered data and to provide research input to studies on combustion emissions and health effects since trace elements in fuels can be emitted into the atmosphere during combustion. The information will also be used to develop emission factors to detect potentially toxic components introduced through contamination, and to provide a mechanism for enforcing Federal fuel additive standards (such as lead and phosphorous limits in gasoline). Samples collected in the 1972 operation were predominantly gasoline, although a limited number of samples of other types of fuels and fuel additives was collected. Trace analytical methods used included neutron activation, spark source mass spectrometry, isotope dilution, atomic absorption including carbon rod atomizer, anodic stripping voltammetry, isotope separation techniques, and lead screening techniques. Impact on the environment is discussed.

DO NOT  
USE →

INTERLABORATORY EVALUATION OF STANDARD REFERENCE MATERIALS FOR TRACE ELEMENTS IN COAL, FLY ASH, FUEL OIL, AND GASOLINE - Darryl J. von Lehmden (1), Philip D. La Fleur (2), and Gerald G. Akland (1), (1) Environmental Protection Agency, National Environmental Research Center, Research Triangle Park, North Carolina 27711, and (2) U. S. Department of Commerce, National Bureau of Standards, Washington, D. C. 20234

The Environmental Protection Agency and the National Bureau of Standards have jointly conducted an interlaboratory comparison program for trace elements in four standard reference materials. The concentration of fifteen chemical elements was certified by the National Bureau of Standards concurrent with the interlaboratory comparison program. The standard reference materials include coal, fly ash, residual fuel oil and gasoline. The concentrations were certified in these materials for the following elements; mercury, beryllium, lead, cadmium, vanadium, manganese, nickel, chromium, arsenic, selenium, zinc, sulfur, phosphorous, fluorine, and uranium. Over fifty laboratories participated in the interlaboratory comparison program. Chemical element concentrations are reported using neutron activation analysis (radio chemical and instrumental), atomic absorption spectrometry, spark source mass spectrometry (isotope dilution and general scan), X-ray fluorescence, optical emission spectroscopy, and a variety of colorimetric and gravimetric methods. Precision results are reported based on replicate analysis. Accuracy results are reported based on the certified values. Preliminary grouping of the "best" analytical methods for each chemical element in each samples matrix will be described.

## THE FATE OF SOME TRACE ELEMENTS DURING COAL PRETREATMENT AND COMBUSTION

Hyman Schultz, E. A. Hattman, and W. B. Booher

Bureau of Mines, Pittsburgh Energy Research Center,  
4800 Forbes Avenue, Pittsburgh, Pennsylvania 15213INTRODUCTION

Why should we interest ourselves in trace metals in coals? Fact #1: There are a number of elements known to be of high toxicity in coal, most of them present in trace amounts. Fact #2: Over 300 million tons of coal was burned in the United States last year for the generation of electric power. When we put the two facts together, we realize that we are talking of a total of tons; hundreds of tons or even thousands of tons of toxic elements present in the coal we burn for power generation. How much of these toxic elements are present in the coal we burn for power generation? How much of these toxic trace elements enters the environment via the smoke stacks of powerplants?

Today I would like to discuss two trace-element studies being carried out at the Pittsburgh Energy Research Center of the Federal Bureau of Mines. The first program, which is funded by the Bureau, is involved in elucidating the fate of the various toxic trace elements present in coal when the coal is burned in powerplants. The second program is funded by the Environmental Protection Agency and is concerned with investigating the distribution of the trace elements in coal using specific gravity separations to divide the coal into discreet fractions.

The two programs taken together can give us a picture of what happens to the trace elements in coal from the coal bed to the powerplant stack. Both investigations are still in progress, so today's talk is really an interim report. I would like to cover the problems we have encountered, the results we have obtained, and any conclusions we have drawn from the results.

The elements that we are currently studying in the EPA program are mercury, copper, chromium, manganese, nickel, and fluorine. In the Bureau program, studies so far have been limited to mercury, cadmium, and lead.

Let us elucidate some of the general problems one encounters in analyzing coal for its trace element content. Except for the special case of mercury, there is no standard coal presently available for use in trace-element analysis. Because the precision and accuracy of the analytical procedures used are in many cases affected by the matrix one is dealing with, the lack of a standard coal is a serious problem.

Contamination is another problem one encounters in trace analysis. Mercury is ubiquitous in many laboratories as is fluoride. Lead is present in dust particularly if your laboratory is close to automobile traffic.

EXPERIMENTAL APPROACH

A. Coal pretreatment study. Selected coals were crushed and separated in organic fluids of known specific gravity. The head (i.e., starting) coal and each specific gravity fraction were analyzed for the trace element or elements being studied and their distribution noted.

B. Combustion study. Coal was combusted in a 100-g/hr combustor, and the ash and flue gases were collected and analyzed for the trace element being studied. After completion of the initial study with the 100-g/hr combustor, coal and ash were obtained from a 500-lb/hr furnace and finally from commercial powerplants. The samples were analyzed

for the trace elements being studied, and the maximum amount of the element that could be released was calculated.

#### ANALYTICAL METHODS

A. Mercury. Mercury is determined in coal by means of a double gold amalgamation-flameless atomic absorption procedure. Because mercury is volatile and can thus be quantitatively separated from the coal matrix, calibration can be accomplished with mercury-saturated air. Mercury is the only trace element for which there is presently an NBS certified standard coal. We normally use mercury-saturated air for calibration purposes on a day-to-day basis and periodically analyze the NBS standard coal in order to check our procedure. Table 1 shows some of the results we have obtained with the NBS standard coal.

Table 1  
Analysis of NBS SRM No. 1630  
NBS certified mercury value =  $0.126 \pm 0.006$  ppm Hg

<u>Dates</u>	<u>Number of replicates</u>	<u>Bureau value</u>
2/24/72	5	0.12 $\pm$ 0.02
4/19/72	5	.12 $\pm$ .01
7/5/72	6	.14 $\pm$ .02
9/24/72 through 12/13/72	39	.13 $\pm$ .03
2/1/73 through 3/2/73	37	.13 $\pm$ .02

As you can see, agreement is very good.

B. Fluorine. Fluorine in coal is determined by combusting the coal in the presence of calcium oxide, fusing the residue with  $\text{Na}_2\text{CO}_3$ , leaching the melt with phosphoric acid, distilling the solution with  $\text{H}_2\text{SO}_4$ , concentrating the fluoride by passing the solution through an anion exchange resin (Amberlite IRA 410), and determining the fluoride content of the solution with a fluoride specific ion electrode. An NBS opal glass standard is frequently carried through the entire procedure to check fluorine recovery.

C. Copper, chromium, manganese, and nickel. The analytical method for the determination of copper, chromium, manganese, and nickel involves digestion of the coal with  $\text{HNO}_3$  and  $\text{HClO}_4$ , fusion of the residue with lithium metaborate, and determination of the combined digestion and leach solutions by atomic absorption spectrophotometry. Since there is no standard material to analyze for the construction of calibration curves, the method of standard additions is employed for the assay. While the method of standard additions does increase the time required for the analysis, it eliminates the effect of the matrix.

D. Cadmium and lead. Cadmium and lead are determined in coal by ashing the coal at  $500^\circ\text{C}$ , treating with HF and HCl, fusing the residue with  $\text{K}_2\text{CO}_3$ , evaporating to near dryness, dissolving in HCl, adding KI and ascorbic acid, extracting into MIBK, and analyzing for Pb and Cd by means of atomic absorption. Blanks are carried through the entire procedure, and the method of standard additions is used for calibration.

RESULTS

A. Mercury. An Indiana V strip coal from Indiana and a Lower Kittanning strip coal from Pennsylvania were separated into four specific-gravity fractions and analyzed for their trace mercury content. The results are shown in tables 2 and 3. It is clear that mercury tends to concentrate in the mineral matter and probably exists in coal as an inorganic compound.

Table 2  
Coal - Lower Kittanning Bed, Pennsylvania, strip coal  
Mercury content of coal = 0.26 ppm

<u>Specific gravity</u>	<u>Weight-percent</u>	<u>Mercury content, ppm</u>	<u>Percent of total mercury in fraction</u>
Float - 1.30	20.0	0.16	12
1.30 - 1.40	28.1	.23	25
1.40 - 1.60	24.8	.19	18
Sink - 1.60	27.1	.43	45

Table 3  
Coal - Indiana V Bed, Indiana, strip coal  
Mercury content of coal = 0.13 ppm

<u>Specific gravity</u>	<u>Weight-percent</u>	<u>Mercury content, ppm</u>	<u>Percent of total mercury in fraction</u>
Float - 1.30	42.6	0.08 ±0.03	29 ±11
1.30 - 1.40	36.3	.07 ±.03	22 ±9
1.40 - 1.60	13.7	.15 ±.03	15 ±3
Sink - 1.60	7.4	.59 ±.05	34 ±3

Table 4  
100-g/hr combustor: Summary of results

<u>Coal</u> <sup>4/</sup>	<u>Run</u>	<u>Combustion feed rate, g/hr</u>	<u>Efficiency, percent</u>	<u>Fly ash production rate, g/hr</u>	<u>Mercury content (±1 standard deviation)</u>			<u>Total mercury in fly ash, percent</u>	<u>Total mercury accounted for, percent</u>
					<u>Coal, <math>\mu\text{g/g}</math></u>	<u>Fly ash, <math>\mu\text{g/g}</math></u>	<u>Flue gas, <math>\mu\text{g}/\text{m}^3</math></u> <sup>3/</sup>		
DRB-E	1	98.1	97.6	9.1	1/ 0.15±0.02	0.97±0.05	2.2	60	77
DRB-E	2	105.1	97.0	10.4		.83±.13	6.5	55	101
DRB-E	3	108.1	96.4	11.3		.95±.09	1.7	66	78
P-3	1	98.9	97.5	23.8	2/ .24±.05	.31±.04	7.4	31	62
P-3	2	135.7	96.3	34.3		.35±.06	(3/)	37	(3/)
P-3	3	117.2	98.3	27.1		.37±.04	14.4	36	94

<sup>1/</sup> Average value of 12 replicates for DRB-E.

<sup>2/</sup> Average value of 21 replicates for P-3.

<sup>3/</sup> No flue gas sampling on this run.

<sup>4/</sup> DRB-E is a washed deep-mined Pittsburgh seam coal originating in Washington County, Pa. P-3 is a mixture of Tebo seam and Weir seam coals from Henry County, Mo.

Table 4 shows the results obtained with the 100-g/hr combustor. Table 5 shows the results obtained with the 500-lb/hr combustor. Table 6 shows the analyses of the coals used in the combustion experiments with the 100-g/hr and 500-lb/hr combustors. Table 7 shows the results obtained with power plant samples. The terms MR, DRB-E, and P-3 are those employed by the engineers running the combustors to identify series of runs under slightly different conditions but using the same coal.

Table 5  
500-lb/hr combustor: Summary of results

Mercury in coal (MR) <sup>1/</sup> .....	μg Hg/g coal .....	0.18 <sup>±</sup> 0.04
Number of replicates .....		23
Mercury in fly ash .....	μg Hg/g ash .....	0.22 <sup>±</sup> 0.04
Number of replicates .....		17
Percent of total mercury found in fly ash .....		12 <sup>±</sup> 3

<sup>1/</sup> MR is a Pittsburgh seam coal from Pennsylvania.

Table 6  
Analysis of coals combusted (mf basis)

	<u>DRB-E</u>	<u>P-3</u>	<u>MR</u>
Proximate analysis, weight-percent:			
Volatile matter .....	35.8	37.8	37.7
Fixed carbon .....	57.3	40.6	52.2
Ash .....	6.9	21.6	10.1
Ultimate analysis, weight-percent:			
Hydrogen .....	5.1	4.4	5.0
Carbon .....	78.1	61.9	74.2
Nitrogen .....	1.6	1.0	1.5
Oxygen .....	7.1	5.9	7.1
Sulfur .....	1.2	5.2	2.1
Ash .....	6.9	21.6	10.1
Calorific value, Btu .....	13,970	11,190	13,310
Free swelling index .....	8	2.5	1.5

Table 7  
Summary of powerplant data

<u>Type of firing</u>	<u>Steam conditions</u>			<u>Coal fired</u>	<u>Fly ash sample collection conditions</u>	<u>Mercury content of the fly ash, μg Hg/g</u>
	<u>Rate, 10<sup>3</sup> lb/hr</u>	<u>Pressure, psig</u>	<u>Temperature, ° F</u>			
Slag top	702	1,268	899	Illinois No. 6 hvcb.	Mechanical collector hopper	0.10 <sup>±</sup> 0.02
Slag top	723	1,293	799	Illinois No. 6, hvcb.	Electrostatic precipitator hopper	.26 <sup>±</sup> .04
Dry bottom	461	1,450	928	Kentucky No. 6, hvbb.	Mechanical dusty collector hopper	.22 <sup>±</sup> .02

Based on mercury analyses for Illinois No. 6 coal published by the Illinois Geological Survey, the average percentage of the mercury in the original coal accounted for in the ash is 13 percent.

The results seem to indicate that as only 10 to 15 percent of the mercury is retained by the fly ash, 85 to 90 percent of the mercury in the coal could be emitted via the powerplant smoke stacks.

B. Lead and cadmium. The results obtained for cadmium and lead are limited and of a preliminary nature. The longer time required for each analysis and the problems of contamination resulted in less replication. As the result of insufficient replication, most of the results reported do not have statistical errors attached (however, each is the average of at least two values).

Table 8 gives the lead and cadmium assays for Pittsburgh seam coal; table 9 gives the concentration of lead and cadmium found in the ashes from combustion experiments. Table 9 also shows the percentage of the lead and cadmium in the coal that was retained by the ash. The conditions under which the coal was burnt varied with each run, particularly with the 500-lb/hr combustor so that the results of individual runs cannot be compared. It should be noted that cadmium and lead are retained to a greater degree in the ash from the 500-lb/hr combustor than was mercury. This of course could be predicted from relative volatilities.

Table 8  
Lead and cadmium content of a  
Pittsburgh seam coal ( $\pm 1$  S.E.)

<u>Lead content,</u> <u>ppm</u>	<u>Number of</u> <u>samples</u>	<u>Cadmium</u> <u>content, ppm</u>	<u>Number of</u> <u>samples</u>
7.7 $\pm 0.5$	9	0.14 $\pm 0.05$	9

Table 9  
Lead and cadmium in fly ash

<u>Combustor</u>	<u>Cadmium in</u> <u>ash, ppm</u>	<u>Cadmium accounted</u> <u>for, percent</u>	<u>Lead in</u> <u>ash, ppm</u>	<u>Lead accounted</u> <u>for, percent</u>
100 g/hr	1.0	68	--	--
100 g/hr	.74	54	71	92
100 g/hr	.99	76	68	93
500 lb/hr	1.22	101	49	72
500 lb/hr	.78	65	44	64
500 lb/hr	.36	37	25	46

C. Copper, chromium, manganese, and nickel. Efforts aimed at defining the behavior of Cu, Cr, Mn, and Ni during specific gravity separation and combustion of coal are in a very preliminary stage. Efforts to date have been aimed at optimizing the analytical procedures and locating and eliminating sources of contamination. One interesting preliminary result presented in table 10 seems to indicate that crushing coal adds significant amounts of manganese to the coal. The jaws of the crushing apparatus were made of a manganese steel. The coal used was a strip coal from the Lennox Bed in Colorado.

Table 10  
Analysis of coal before and after crushing, ppm

<u>Element</u>	<u>Concentration before crushing</u>	<u>Concentration after crushing</u>
Cr	3.4	4.3
Cu	3.2	5.4
Mn	4.1	10.3

D. Fluorine. Efforts aimed at analyzing coals for fluorine have been stymied by contamination problems. Sources of fluorine contamination have been located in phosphoric acid, calcium oxide, boiling chips, and teflon-covered stirring bars. Extreme care must be taken in the selection of storage containers, and the history of the distillation apparatus should be known. We believe that we have now located the sources of error in the fluoride analysis and are in the process of analyzing series of float-sink samples for their fluoride content.

#### SUMMARY AND CONCLUSIONS

Our efforts with trace elements in coal have to date met with varying degrees of success, but certain important conclusions can be drawn from our findings.

First, it would appear that as much as 40 percent of the mercury in the coal is associated with the high specific gravity fraction of the coal. Thus if the pyrite is removed from coal to lower sulfur emissions, a substantial part of the mercury in the coal is also removed at no extra cost. Second, about 10 to 15 percent of the mercury from the coal may remain with the fly ash in coal-burning powerplants. Taking both factors into account could reduce the maximum emission of mercury to about 50 percent of that present in the coal.

Cadmium and lead are less volatile elements than mercury. As one would expect, the experimental evidence indicates that they are retained in the fly ash to a greater extent than is the mercury. As the program continues, other elements that are even less volatile than lead and cadmium will be investigated, and one would expect them to be retained in the fly ash to an even greater extent than are lead and cadmium.

Our experience with fluorine, copper, manganese, chromium, and nickel emphasizes the difficulties inherent in doing trace analyses in matrices as complex as coal. While care must be exercised in performing any chemical analysis, trace analysis requires extreme vigilance. In addition to the care required in trace analyses, our studies have shown that the coal handling procedures themselves may add trace elements to the coal.

TRACE ELEMENT MASS BALANCE  
AROUND A COAL-FIRED STEAM PLANT\*N. E. Bolton, J. A. Carter, J. F. Emery, C. Feldman,  
W. Fulkerson, L. D. Hulett, and W. S. LyonOak Ridge National Laboratory\*\*  
Oak Ridge, Tennessee 37830

## 1. Introduction

Toxic elements are present in trace quantities in coal and other fossil fuels. Since the quantities of these fuels consumed each year are enormous, the associated quantities of potentially harmful toxic elements are also appreciable. For example, assuming 600 million tons of coal burned per year in the United States, with average concentrations\*\*\* for Hg of 0.10 ppm, Pb-20, Cd-0.4, As-5, Se-5, Sb-4, V-25, Zn-200, Ni-100, Cr-20, and Be-2, the corresponding tonnages of the elements are: Hg-60, Pb-12,000, Cd-240, As-3000, Se-3000, Sb-2400, V-15,000, Zn-120,000, Ni-60,000, Cr-12,000, and Be-1200.

An appreciable fraction (62%) of the coal consumed is burned at central power stations, so it is important to know the fate of potentially hazardous trace elements at such plants. The purpose of this work is to determine the fate of trace elements in coal associated with generation of electricity at a large central power station. The study involves two complementary activities: (1) a mass balance for trace elements through the plant as obtained by in-plant sampling, and (2) measurements of the elements in the surroundings to estimate the effect of emissions on the concentration of toxic elements in air, soil, plant life, and in the water, sediment, and biota of the stream receiving the ash pond runoff. This paper deals with the in-plant portion of the work, which is a collaborative effort between ORNL and TVA.

The power station at which the study was made is the Thomas A. Allen Steam Plant in Memphis, Tennessee, which has an 870 MW(e) peak capacity from three similar cyclone fed boilers. The plant is part of the TVA power system, and it was chosen because the Number 2 Unit was being renovated with addition of a new Lodge Cottrell electrostatic precipitator so the TVA Power Production Division test sampling crew were available to help sample during compliance testing of the precipitator.

## 2. Sampling and Methods of Analysis

Figure 1 shows the sampling points on a schematic of the Number 2 Unit. Samples taken at locations Number 1 and 2 were composite samples of the coal entering the boiler, and of the slag material leaving the boiler, respectively. At location Number 3 the inlet air being supplied to the boiler was sampled. At locations 4 and 5 a series of samples were taken isokinetically at various locations in the ducts before and after the electrostatic precipitator, respectively; and at location 6 a series of samples were taken isokinetically in the stack at approximately 82 m above ground level.

The large size of the ducts being sampled required specially fabricated sampling

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\* Work supported by the National Science Foundation RANN Program under NSF Interagency Agreement No. AG-398 with the U.S. Atomic Energy Commission.

\*\* Operated by Union Carbide Corporation for the U.S. Atomic Energy Commission, Contract No. W-7405-eng-26.

\*\*\* These concentrations are representative of values measured for coal burned at the Allen Steam Plant.

probes and special probes equipped with forward-reverse pitot tubes for determining isokinetic sampling rates. Figure 2 shows how the sampling probe was constructed. The sample is drawn through an alundum thimble at a predetermined isokinetic sampling rate. This thimble is followed by a Gelman fiberglass filter paper holder which collects particles as small as  $0.1 \mu$ . This is essentially the standard ASTM method for sampling gases for particulates.<sup>1</sup> These filters are then followed by the cold trap to bring the flue gas through the dew point very quickly and collect all materials which will condense in a dry trap. Because of the very high concentration of moisture in the flue gas it was necessary to add a dropout glass jar following this cold trap to prevent loss of the condensate. The cold trap and condensate dropout jar were used in an attempt to trap mercury and other condensable vapors from the flue gas sample.

Two probes were fabricated for sampling the precipitator inlet, one for the precipitator outlet and one for the stack. By limiting the number of test points at each plane in the precipitator outlet the average sampling time required to complete a test was about 280 to 300 minutes. The types and numbers of samples collected for each complete run are shown in Table 1. The total number is 24 distinct samples for each complete test run.

Table 1. Types and numbers of samples

Composite Coal Sample - 1
Composite Slag Tank Sample - 1
Precipitator Inlet - 6 thimbles, 2 cold traps, 2 glass papers
Precipitator Outlet - 4 thimbles, 1 cold trap, 1 filter paper
Stack Sample - 2 thimbles, 1 trap, 1 glass paper
Inlet Air - 1 thimble and 1 glass paper

Although the plant is designed to operate at 290 MW per unit, a 240 MW load was chosen for these tests because it was felt that this load could be maintained without interruption during the 5-hour sampling time required to secure our samples. The consumption of coal at this power level is 82.5 tons per hour on a dry weight basis. Sampling of the coal and slag was performed by compositing samples obtained periodically during the course of the test. From the weight of fly ash material collected in the ASTM filter system, the total air volume passed through the thimble, and the velocity of air passing through the system, the total particulate flow rate was calculated. In all, four runs were made, 1 reference test, and 3 for mass balance (runs 5, 7, and 9). A gas velocity traverse was made in the precipitator inlet and outlet ducts just prior to each mass balance run to determine isokinetic sampling rates for each sampling position.

The reference test was performed using the standard ASTM method for determining grain loadings to electrostatic precipitators. This test was used to verify the adequacy of the number of samples secured for mass balance calculations. Comparison of grain loading calculations using TVA standard probes and ORNL fabricated probes show the mass balance samples are, indeed, representative.

Analysis of the samples for elemental constituents was performed using instrumented neutron activation analysis (NAA) and spark-source mass spectrometry (SSMS)<sup>2</sup> In addition, the many Hg determinations were made by flameless atomic absorption (AA).

The NAA technique involved irradiating each dry homogenized sample (0.01 to 0.2 g) in a sealed plastic vial. This vial was placed in a "rabbit" together with

Au and Mn flux monitors and irradiated in the Oak Ridge Research Reactor for a period varying from a few seconds (for short lived radioactive products), to 20 minutes. After irradiation the samples were removed and counted at various set decay times using a Ge(Li) detector and a nuclear-data PDP-15 analyzer computer system. Using programs developed at ORNL, these counting data were processed, and x-ray peaks identified, absolute activities calculated, and from the flux measurement and known nuclear parameters, the  $\mu\text{g/g}$  of each element found was calculated. Results in all cases have a 5-10% uncertainty assignment. The entire process is nondestructive in that no chemical treatment is performed, so there is only a minimal chance of sample contamination or loss.

The flameless atomic absorption method has a reproducibility of about 2% or better for homogeneous specimens. Checks<sup>3</sup> between AA and NAA (with radiochemical separation after irradiation) and isotope dilution spark source mass spectroscopy on thoroughly homogenized tuna fish and Bureau of Mines round-robin coal specimens indicate good agreement between the methods. ( $0.425 \pm 0.9\%$ ,  $0.45 \pm 3.5\%$ , and  $0.45 \pm 4.4\%$  for tuna by AA, NAA, and SSMS, respectively, and 1.004 is the average ratio of NAA to AA results for 5 coal samples.) These results indicate that the technique used in sample preparation for AA did not result in mercury losses since the NAA method is not subject to losses of this type.

Spark-source mass spectrometry (SSMS) is also a multi-element technique; conventionally the data obtained are semi-quantitative and the results have an uncertainty of  $\pm 50\%$  or less. If the stable isotope dilution technique is performed, the SSMS can be  $\pm 3\%$ . This latter technique was used for a few elements: Pb, Cd, and Zn as noted in the tabulations of results. NAA and SSMS complement each other quite well, and those elements for which one technique has poor sensitivity can usually be measured by the other.

### 3. Mass Balance Results

A mass balance for the various elements was calculated using the following equations:

$$Q_C(A) = C_C(A) \times (\text{g coal/min}) \quad (1)$$

$$Q_{P.I.}(A) = C_{P.I.}(A) \times (\text{g fly ash/min}) \quad (2)$$

$$Q_{S.T.}(A) = C_{S.T.}(A) \times (\text{g ash in coal/min} - \text{g fly ash to precipitator/min}) \quad (3)$$

for balance:

$$Q_C(A) = Q_{P.I.}(A) + Q_{S.T.}(A) \quad (4)$$

$$\text{percent imbalance} = \frac{Q_{P.I.} + Q_{S.T.} - Q_C}{Q_C} \times 100 \quad (5)$$

$Q_C(A)$ ,  $Q_{P.I.}(A)$  and  $Q_{S.T.}(A)$  are the flow rates of element A in g/min associated with the coal, precipitator inlet fly ash, and slag tank solids, respectively, and  $C_C(A)$ ,  $C_{P.I.}(A)$  and  $C_{S.T.}(A)$  are the corresponding concentrations of element A in the coal, the fly ash collected in the precipitator inlet, and the slag tank solids. The flow of trace elements into the plant with suspended particulates in inlet air was negligible. We were unable to measure the total solids flow from the slag tank because of the nature of this discharge. (Every four hours the slag tank residue is washed out to the ash pond with 2-4 hundred thousand gallons of water.) For this reason we estimated the slag tank discharge as the difference between ash flow rate in the coal and the total fly ash flow rate. Presuming that this assumption is valid, that the sampling was complete and representative, and that

the analyses are correct, the condition for balance is given by equation 4. To test this we have calculated a percent imbalance from experimental results by equation 5. Also, the precipitator efficiency for an element was calculated by

$$\text{Precipitator efficiency} = \frac{Q_{P.I.}(A) - Q_{P.O.}(A)}{Q_{P.I.}(A)} \times 100 \quad (6)$$

The results of the mass balance calculations for 8 major elements and 22 minor elements for run 9 are given in Tables 2 and 3, together with the corresponding concentrations in the coal, precipitator inlet and outlet fly ash, and in the slag tank solids. A complete tabulation of results for all three runs is given in a progress report of the project<sup>4</sup> and this includes some data for 57 elements.

In general, agreement between the two analytical methods is reasonable. There is a consistent negative imbalance, the average of which was -26% and -16% for NAA and SSMS results, respectively, for the major elements and -1% and -18% for the minor elements. In the averages for minor elements we have excluded the results for Hg and As. In view of the assumptions necessary and the difficulty of obtaining truly representative samples the balance is satisfactory for most elements. Notable exceptions are elements which can be present in a gaseous form. One may be arsenic (Table 3) and another is mercury which is discussed below. One reason for the consistent negative imbalance could be that fly ash samples were taken under steady state conditions. Two operations were not investigated and these might account for this imbalance. The air heaters are cleaned pneumatically once per 8-hour shift, and soot is blown from the boiler tubes about two times per shift. If this material were measured it would increase the average fly ash flow rate ( $Q_{P.I.}$ ). It is not known whether or not these operations can account for a significant percentage of the trace elements. Future in-plant sampling will include these two operations.

As in the case of the slag tank there was no way to quantitatively measure the precipitator residue flow rate. These residues are slurried with water and flushed continuously to the ash pond. However, for all of the elements except selenium the precipitator was extremely efficient (> 95%) as calculated from the inlet and outlet fly ash concentrations using equation 6. The reason that selenium fails to be scavenged effectively is not known and certainly warrants investigation. One possibility is that part of the selenium is in a volatile state but is readily adsorbed on particulates trapped by the alundum thimbles.

Mercury has been determined on virtually every sample (the filters, cold trap and slag tank water and residue). We are unable, however, to find the bulk of the Hg that we know is entering the system via the coal. From this we conclude that Hg is present in the stack gas as a vapor which we were unable to trap.

Table 4 gives all of the values obtained for Hg in coal which range from .057 to .198 ppm, but most values are in the range of 0.07 ppm. Our attempt at a Hg balance for runs 5 and 9 is shown in Table 5. From these numbers it is clear that very little mercury (~ 12%) remains with the slag and fly ash particles. The cold trap was not effective in trapping Hg vapor (~ 11%). The results are in qualitative agreement with those of Billings and Matson,<sup>5</sup> except that these authors were able to collect the Hg in the gas phase. Their data shows that most of the Hg is in the gas phase which can also be implied from our results.

Recently, we returned to the Allen plant and sampled the flue gas using a four impinger train with a pre-scrubber of sodium carbonate to remove the acid gases, followed by three impingers charged with iodine monochloride solution. Preliminary results show that mercury was collected and quantities detected were of the expected magnitude based on Hg concentrations in the coal which we had measured previously. This technique will be used for the Hg balance at the next in-plant sampling.

Table 2. Elemental concentrations and mass balance results for a number of major elements measured for run 9

Element	Method	Concentration (ppm unless otherwise indicated)			Mass Flow (g/min)			Precipitator Efficiency (%)
		Coal	S.T. <sup>a</sup>	P.I. <sup>a</sup>	Coal	S.T. <sup>a</sup>	P.I. <sup>a</sup>	
Al	NAA	1.06%	6.6%	6.9%	$1.3 \times 10^4$	$7.2 \times 10^3$	$3.4 \times 10^3$	68
	SSMS	1%	5%	10%	$1.3 \times 10^4$	$5.5 \times 10^3$	$7.3 \times 10^3$	-1
Ca	NAA	0.38%	2.7%	1.4%	$0.47 \times 10^4$	$3.0 \times 10^3$	$6.8 \times 10^2$	-22
	SSMS	0.5%	3%	3%	$0.6 \times 10^4$	$3.3 \times 10^3$	$1.5 \times 10^3$	-20
Fe	NAA	1.3%	10.1%	9.3%	$1.6 \times 10^4$	$1.1 \times 10^4$	$4.5 \times 10^3$	-3.1
	SSMS	2%	10%	10%	$2.5 \times 10^4$	$1 \times 10^4$	$5 \times 10^3$	-40
K	NAA	0.22%	0.95%	1.65%	$0.27 \times 10^4$	$1.0 \times 10^3$	$8.0 \times 10^2$	-33
	SSMS	0.06%	0.5%	0.7%	$0.07 \times 10^4$	$5 \times 10^2$	$3 \times 10^2$	+14
Mg	NAA	0.17%	0.41%	0.53%	$0.21 \times 10^4$	$4.5 \times 10^2$	$2.7 \times 10^2$	-66
	SSMS	0.15%	0.7%	0.4%	$0.18 \times 10^4$	$8 \times 10^2$	$3 \times 10^2$	-39
Mn	NAA	54	418	323	67	46	16	-7.5
	SSMS	100	1000	700	130	110	34	11
Na	NAA	0.069%	0.32%	0.7%	860	350	340	-20
	SSMS	0.03%	0.2%	0.3%	370	220	150	0
S	NAA	5.1%	30%	10.5%	$6.4 \times 10^4$	$3.3 \times 10^4$	$1.5 \times 10^4$	-24
	SSMS	5%	3000	3700	890	330	180	-43
Ti	NAA	710	3000	2500	880	220	240	-48
	SSMS	700	2000	1000	880	220	240	-48

<sup>a</sup>S.T., P.I., and P.O. are abbreviations for slag tank solids, precipitator inlet, and precipitator outlet, respectively.

Table 3. Elemental concentration and mass balance results for a number of minor elements measured for run 9

Element	Method	Concentration (ppm)			Mass Flows (g/min)					Precipitator Efficiency (%)	
		Coal	S.T. <sup>a</sup>	P.I. <sup>a</sup>	P.O. <sup>a</sup>	Coal	S.T. <sup>a</sup>	P.I. <sup>a</sup>	Imbalance (%)		P.O. <sup>a</sup>
As	NAA	3.8	0.5	46	50	4.7	0.05	2.2	-52	0.1	95
	SSMS	5	2	40	20	6.2	0.2	2	-64	0.04	98
Ba	NAA	79	600	1700	100	130	33	83	-11	0.2	99+
	SSMS	<5	<10	17	<10	<6.3	<1.1	0.83	+8.5	<0.02	98
Be	ID <sup>b</sup>	0.47	-3	5.8	0.31	0.59	0.31	0.33			
	SSMS	0.5	2	<10	7	0.63	0.22	<0.5	-1.0	0.014	<96 <sup>c</sup>
Co	NAA	3.3	19	25	58	4.1	2.1	4.4	-19	0.11	91
	SSMS	7	40	70	40	9	4.4	3.4	-13	0.08	96
Cr	NAA	21	180	356	300	26	20	17	42	0.6	96
	SSMS	30	<200	70	40	37	<22	3.4		0.08	98
Cs	NAA	1.5	8	21	4	1.9	0.88	1.02	0	0.008	99+
	SSMS	50	200	400	400	63	22	19	-35	0.8	96
Eu	NAA	0.17	1.4	1.8		0.21	0.15	0.09	14		
	SSMS	~1				~1					
Hg	AA	0.063	0.09	0.043		0.079	0.0099	0.0021	-85		
	NAA	5.0	42	32		6.3	4.6	1.5	-3		
La	SSMS	~10				~10					
	SSMS	25	200	300	200	31	22	15	19	0.4	97
Mo	NAA	20				25					
	SSMS	20	80	200	20	25	8.8	9.7	-26	0.04	99+
Ni	SSMS	<100	500	500	1000	<130	55	24		2	92
	ID <sup>b</sup>	7.4	-4	149		9.25	0.42	8.60	-3		
Pb	SSMS	<20	3	250	100	<25	0.3	12		0.2	98 <sup>c</sup>
	NAA	<1	<0.2	3.2		<0.75	<0.02	0.2			
Sb <sup>d</sup>	SSMS	8	7	10	10	0.8	0.5	0.5		0.02	96
	NAA	3.2	22	25	10	4.0	2.4	1.2	-10	0.02	98
Sc	NAA	3.2	14	<32-48	760	4.0	1.5	<1.5-2.3	<-25 to -5	1.4	7 to 39
	SSMS	6	20	200	7.5	2.2	1.0		-58	0.4	60
Sr <sup>e</sup>	SSMS	20	200	20	20	25	20	1.4	-14	0.04	97
	NAA	3	20	18	3	3.7	2.2	0.87	-17		
Tl	SSMS	<2	2	40	30	<2.5	0.2	1.9			
	NAA	1.67	14	17	7	2.1	1.5	0.83	11	0.014	98
U	NAA	21	125	200	63	26	14	9.7	-9	0.12	99
	SSMS	30	100	350	100	37	11	17	-24	0.2	99
Zn	ID <sup>b</sup>	94	~20	1500		117	2.1	86	-24		
	SSMS	85	100	3000	900	110	11	150		1.7	98 <sup>c</sup>

<sup>a</sup>S.T., P.I., and P.O. stand for slag tank solids, precipitator inlet, and precipitator outlet, respectively.<sup>b</sup>Data obtained by isotope dilution mass spectrometry for composite samples from runs 5 and 9.<sup>c</sup>Precipitator efficiencies calculated on the basis of P.O. by SSMS for run 9 and P.I. by ID from the composite sample runs 5 and 9.<sup>d</sup>Run 5 data.<sup>e</sup>Run 7 data.

Table 4. Hg in coal as determined by atomic absorption

Sample	Date	Hg( $\mu\text{g/g}$ )		
2 ECS 24	26 Jan	0.057		
5 CS 24 AM	28 Jan	0.064	0.063	
5 CS 24 PM	28 Jan	0.069	0.058	
7E CS 26 AM	31 Jan	0.198		
7E CS 26 PM	31 Jan	0.169	0.148	0.136
9E CS 16 AM	1 Feb	0.076	0.060	
9E CS 16 PM	1 Feb	0.060	0.058	
10E CS 19 AM	2 Feb	0.068		
10E CS 19 PM	2 Feb	0.073		
11E CS	3 Feb	0.060		

Table 5. Hg balance

Material	Average Flow g/day	Hg $\mu\text{g/g}$	Hg Flow g/day
Run 5			
Coal	$1.8 \times 10^9$	0.064	115
Ash (Slag)	$1.43 \times 10^8$	0.07	10
Precipitator Inlet	$0.96 \times 10^8$	0.04	4
H <sub>2</sub> O to Ash Pond	$2.9 \times 10^9$	0.003	9
Gas (Cold Trap)	$4.3 \times 10^{10}$	0.0003	13
Run 9			
Coal	$1.8 \times 10^9$	0.064	115
Ash (Slag)	$1.58 \times 10^8$	0.09	14
Precipitator Inlet	$0.70 \times 10^8$	0.043	3
H <sub>2</sub> O to Ash Pond	$2.9 \times 10^9$	0.001	3
Gas (Cold Trap)	$4.4 \times 10^{10}$	0.0003	13

#### 4. Fly Ash Particle Characterization

Figure 3 shows scanning electron photomicrographs of fly ash particles from the precipitator inlet and outlet and from the stack. The particles are predominantly spherical and there is considerable agglomeration of small particles (submicron size) to large ones. Also, there appears to be a fuzzy material present which might be a sulfur compound. Preliminary evidence for this is scanning electron microscope fluorescence analyses of some of the larger particles deposited from the precipitator inlet flue gas on the first stage of a Cassella cascade impactor. Figure 4 shows such an analysis. All of the fluorescence lines, except aluminum, can be attributed to the particles. Since the particles were collected on an aluminum foil the aluminum peak is due primarily to the foil. Upon ion etching by bombardment with argon ions, the sulfur peak decreased substantially indicating sulfur was present primarily on the surface of the particles. As one would expect, the preliminary evidence is that the fly ash particles are a complicated mixture of the elements.

Work is still in progress on determining the particle size distribution in the flue gases before and after the precipitator, and in the stack. Also, composition of fly ash as a function of particle size is in progress.

#### 5. Conclusions

Trace element mass balance measurements around the Number 2 Unit of the coal-fired Allen Steam Plant in Memphis yielded a respectable balance for many elements. However, the results showed a consistent negative imbalance. This might be due to the fact that soot blowing and air heater cleaning operations were not taken into account in the sampling. Because the method of flue gas sampling was designed primarily to collect particulates efficiently, good balances were not obtained for elements forming volatile compounds. For example, more than 80% of the mercury entering with the coal is emitted with the flue gas as a vapor. The large imbalance for arsenic (-58%, Table 3) indicates that a substantial portion of this element is also in the vapor phase of the flue gas.

The electrostatic precipitator was very efficient ( $\sim 98\%$ ) for most trace elements based on analyses of the fly ash particulate specimens collected from the precipitator inlet and outlet. An exception was selenium. Although a reasonable mass balance was obtained for this element (see NAA results, Table 3), it was not removed efficiently by the precipitator. This may indicate that a significant fraction of the material is in the vapor phase in the flue gas, and that it is being adsorbed in

passing through the alundum thimble filter used to sample the fly ash. Accounting more completely for the volatile trace elements such as Hg, Se, and As remains the most significant question still to be answered in future mass balance work.

#### 6. Acknowledgements

The authors wish to express their appreciation to the following personnel of the Tennessee Valley Authority without whose assistance this study could not have been accomplished: Mr. Joseph Greco, Chief Plant Engineering Branch, Division of Power Production; Mr. John H. Lytle, Plant Engineering Branch, who supervised the field test crew during the mass balance runs; and, Dr. Lucy E. Scroggie, Supervisor of the Industrial Hygiene Laboratory, who coordinated TVA's contribution in this joint study for Dr. F. E. Gartrell, Director of Environmental Planning.

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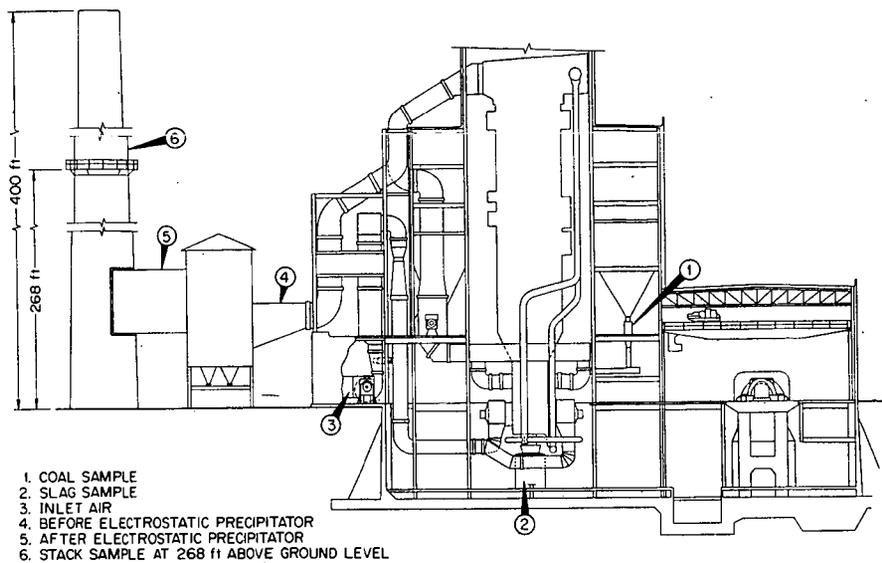


Fig. 1. Schematic of Number 2 Unit, Allen Steam Plant, Memphis.

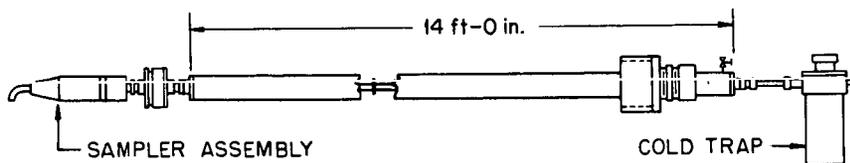


Fig. 2. Schematic of Sampling Probe Used for Mass Balance Study.

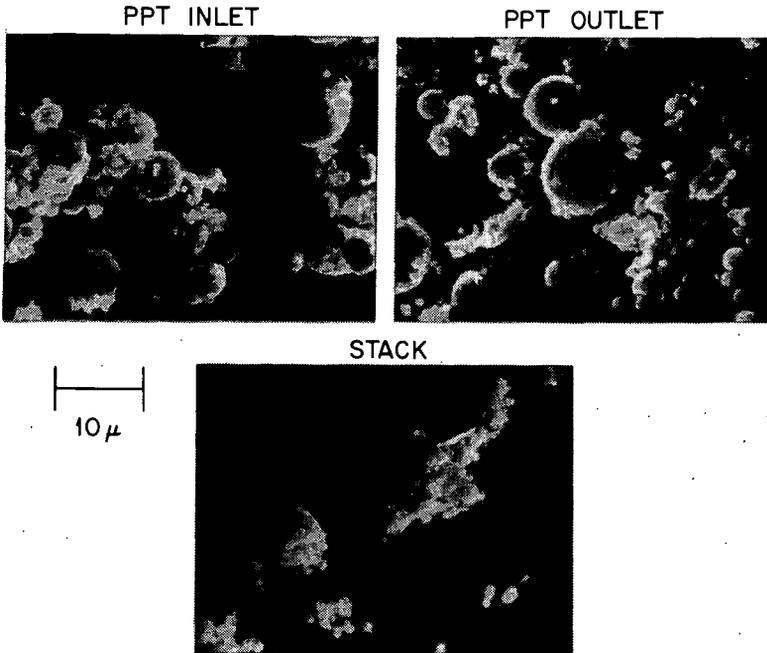


Fig. 3. Scanning Electron Photomicrographs of Fly Ash Particulates Collected on Alundum Thimbles Used to Sample the Precipitator Inlet and Outlet and the Stack.

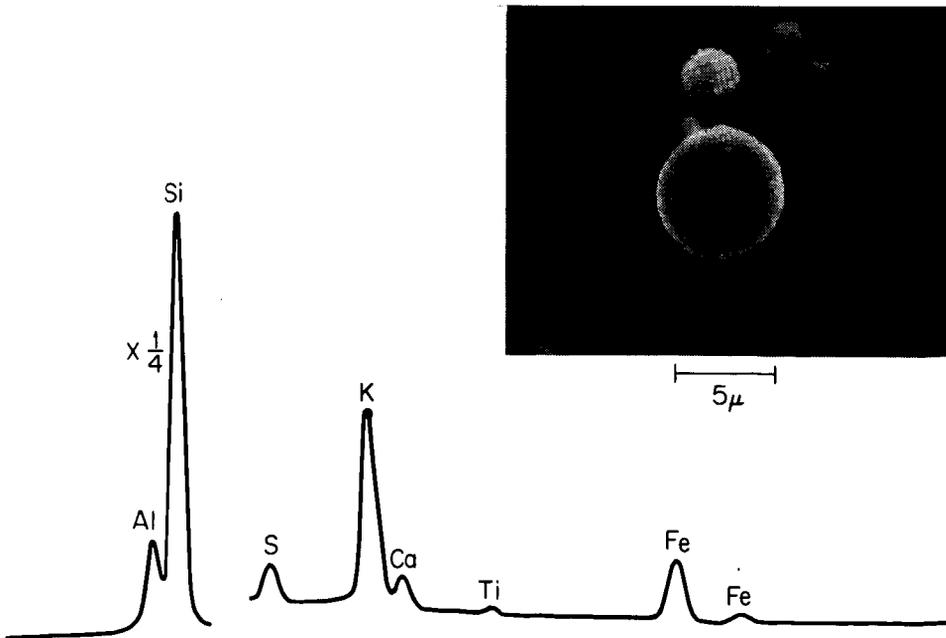


Fig. 4. Qualitative Fluorescence Analysis of a 5  $\mu$  Fly Ash Particle Trapped on the First Stage of the Cassella Cascade Impactor Used to Sample the Precipitator Inlet.

REACTIONS OF ALKALI METAL COMPOUNDS DURING COAL GASIFICATION FOR ELECTRIC POWER GENERATION.\* Sven A. Jansson, Westinghouse Research Laboratories, Pittsburgh, Pa., 15235.

Alkali metal compounds cause hot corrosion and fouling in gas turbines. The extent of alkali release during gasification of coal depends largely on the chemical composition of alkali compounds in coal and on the chemical reactions of these compounds in the coal gas environment. This paper describes results from a study of alkali metal reactions during different steps of the gasification process. Thermochemical calculations and diagrams are used to determine the probable reaction processes, the nature of any volatile alkali metal species, and the composition of solid or liquid reaction product ash components. The calculations show that chlorine promotes alkali release through the formation of highly volatile alkali chlorides. Hydrogen chloride is another important reaction product. As the coal gas is burned with air and expanded through a gas turbine, the alkali chlorides react with sulfur compounds in the gas to form sulfate deposits.

Calculations have been made to determine the effects of different levels of alkali metal, sulfur, and chlorine on condensation temperature and the nature of turbine deposits.

\*Work partially supported under contract with the Office of Coal Research.

State of Trace Elements of Coal During Gasification, A. Attari and J. C. Pau,  
Institute of Gas Technology, 3424 South State Street, Chicago, Illinois 60616

A preliminary study has been initiated (under EPA sponsorship) to determine the concentration of some 35 trace elements in coal with particular emphasis on their fate and distribution among the various solid, liquid, and gaseous effluents of HYGAS pilot plant, now under operation at the Institute of Gas Technology. Coal and solid residue samples were obtained from the pretreatment, hydrogasification, and electrothermal stages of bench-scale development unit of the HYGAS plant. The samples were dry ashed in an oxygen plasma low-temperature asher and the resulting ash samples were decomposed with HF, then dissolved in perchloric acid for subsequent analysis by various atomic absorption methods, except for mercury, which was determined by a combustion-nonflame-AA method. Thus far, Sb, As, Be, Cd, Cr, Pb, Hg, Ni, Se, Te, and V levels have been measured in feed and solid residues of a bituminous coal and the results show substantial removal of elements such as As, Cd, Pb, Hg, Se, and Te during gasification. These results, however, are based on a limited number of samples and further work is in progress to analyze a larger number of samples before any firm conclusions can be drawn.

Coal Gasification for Electric Power Generation - Process Conditions Effecting Contaminant, D. H. Archer, J. L. P. Chen, E. F. Sverdrup, R. W. Hornbeck, Westinghouse Research Labs, Beulah Road - Churchill Boro, Pittsburgh, Pa. 15235.

A coal gasification process has been proposed to provide fuel for electric power generation in a gas and steam turbine combined cycle power plant. The process uses multistaged fluid beds with countercurrent gas and solids flow to produce a low cost plant capable of economically gasifying a wide range of coals. The plant is being designed to meet stringent air pollution standards. It employs a high temperature dolomite sorbent bed for desulfurization. Both coal and dolomite particles are followed through the gasification process to establish the gas compositions, residence times, and temperatures that will effect the release of contaminants. Using these process conditions, a companion paper estimates the release of the alkali metal compounds which are potentially harmful to the turbine.