

TRACE IMPURITIES IN FUELS BY ISOTOPE DILUTION MASS SPECTROMETRY

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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.⁽¹⁾ In fly ash and coal samples, Fe was determined chemically so the isotopes of Fe could be used as an internal standard.⁽²⁾ 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.⁽³⁾ The general method of isotope dilution has been described by Hintenberger.⁽⁴⁾ 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}Cd . The solid line at position 106 represents the ^{106}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}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⁽⁵⁾ and modified at ORNL. The addition of an electrostatic third stage increased the abundance sensitivity to 10^8 as described by Smith et al.⁽⁶⁾

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,⁽⁷⁾ used in conjunction with a sample wheel arrangement,⁽⁸⁾ 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}U and ^{204}Pb .

Pb Analysis by TEMS. Lead analyses are made utilizing the gel technique described by Cameron et al. 1969.⁽⁹⁾ 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}Pb and ^{235}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 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 HNO_3 . After the organic phase is scrubbed with 4 M 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 HNO_3 for analysis.

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

The wet chemical procedure consisted of refluxing first with HNO_3 until the initial reaction subsided, then 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 HNO_3 and loaded onto Re filaments for M.S.

In the bromine method, Br_2 in 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 $\sim 1 \text{ M}$ 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 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⁽¹¹⁾ 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 ± 50 percent, while the isotope dilution measurements are limited by the emulsion detector to ± 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 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 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.

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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) Br_2 oxidation with TEMS.

Table III

IMPURITY MASS FLOW IN A STEAM PLANT
(Flow rate in 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 ^a	0.63	0.30	0.28	- 7.9
Cu	63	22	19	-35
Pb ^a	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 ^a	110	2.0	100	- 7.3
Hg ^a	0.08 ^b	0.007 ^b	0.007	*

^a Isotope dilution; ^b Atomic absorption; ^c 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}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

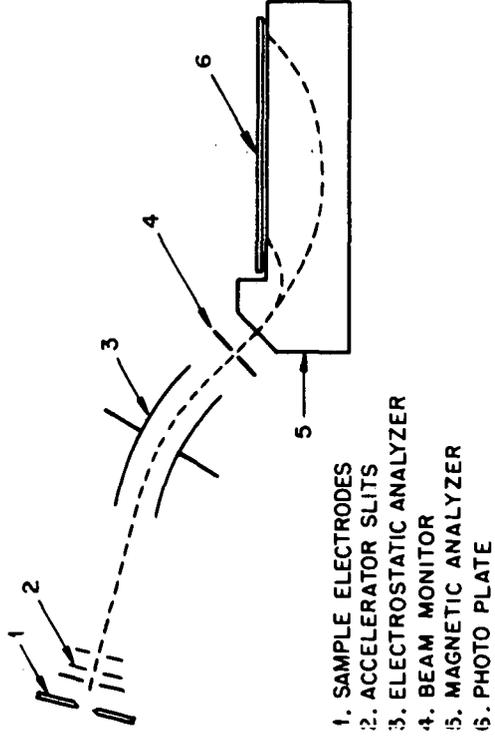
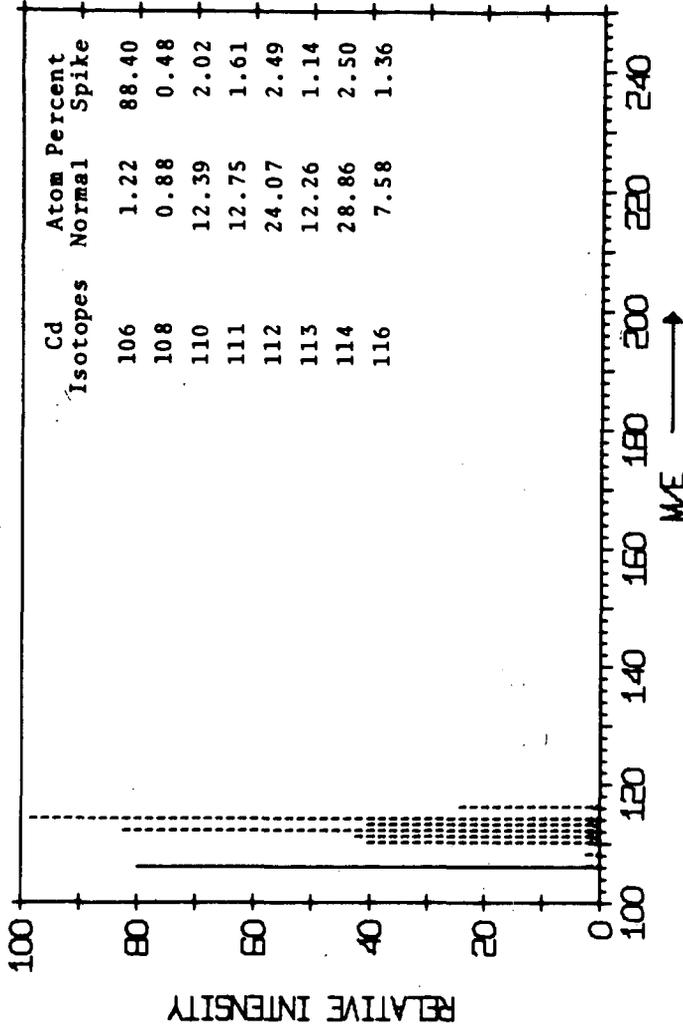


Figure 1. Schematic Diagram of a Double Focusing Spark-Source Mass Spectrometer

ORNL-DWG. 73-3116

Figure 2. Computer Plot of a Cadmium Spectrum Spiked with Enriched ¹⁰⁶Cd

ORNL-DWG. 70-9157

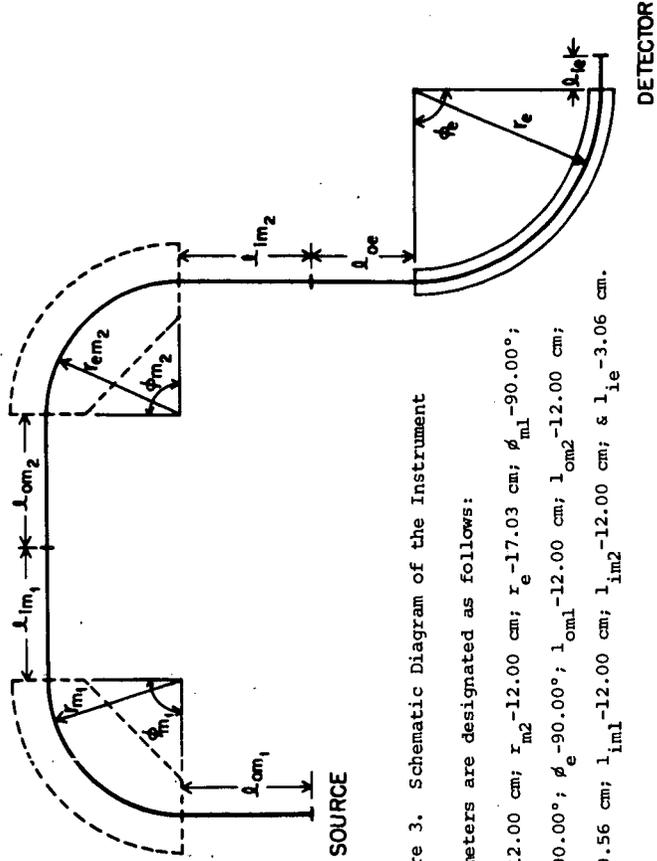


Figure 3. Schematic Diagram of the Instrument

Parameters are designated as follows:

- r_{m1} -12.00 cm; r_{m2} -12.00 cm; r_e -17.03 cm; ϕ_{m1} -90.00°;
 ϕ_{m2} -90.00°; ϕ_e -90.00°; l_{cm1} -12.00 cm; l_{om2} -12.00 cm;
 l_{im1} -12.00 cm; l_{im2} -12.00 cm; l_{ie} -3.06 cm.

ORNL - DWG. 73 - 3118

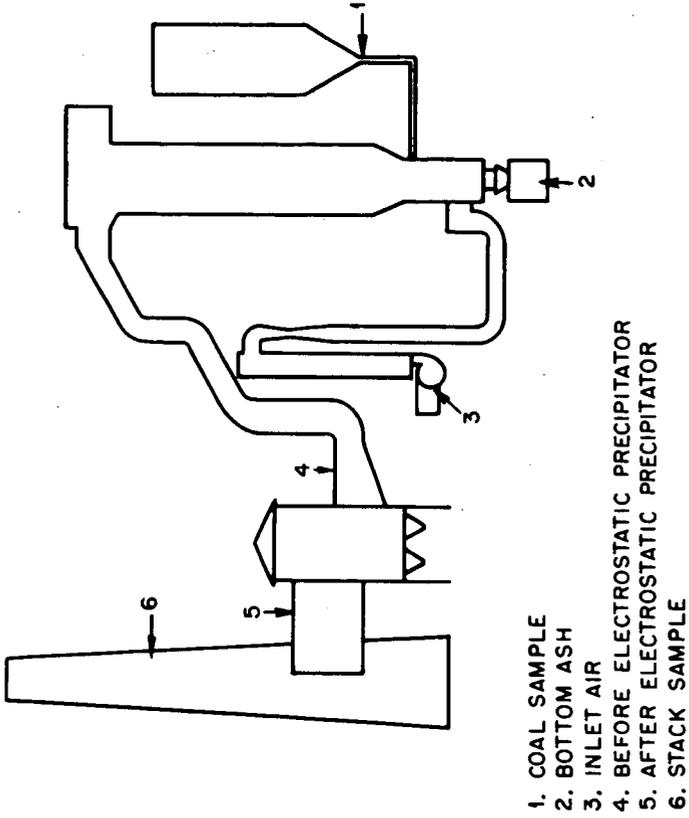


Figure 4. Schematic Diagram of a TVA Coal-Fired Steam Plant