TRACE METAL ANALYSIS IN COAL BY MULTIELEMENT ISOTOPE DILUTION SPARK SOURCE MASS SPECTROMETRY

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INTRODUCTION

The use of spark source mass spectrometry for the analysis of environmentally important elements found in coal and fly ash is described. Significant improvement in the accuracy and precision of the method has been accomplished by use of isotope dilution methods for several elements in a sample. As many as 20 elements have been simultaneously determined in certain energy-related samples using multielement isotope dilution SSMS. The precision and accuracy are typically ±5-10% RSD for elements present at greater than 1 part per million in the sample.

For those samples which are difficult to dissolve cleanly, it is not possible to apply the classical isotope dilution technique. Rather, the dry material is mixed with a 'spiked' conducting matrix containing separated isotopes of the elements of interest. This method combines ease of sample handling with certain desirable aspects of separated isotopes—namely their freedom from contamination effects. Here the precision obtained is typically 10-15% RSD and the accuracy depends on the use of appropriate standards.

EXPERIMENTAL

For an isotope dilution analysis, the following steps are taken:

1. Complete dissolution of the sample in a high purity acid (HNO_3, HCl).
2. Addition of accurately standardized separated isotope 'spikes.'
3. Isotopic equilibration by chemical or thermal means.
4. Mass spectrometric analysis.

The important step is number three, because it is assumed that once equilibration has occurred, the separation or concentration steps that follow need not be quantitatively known. It is also assumed that the equilibrated spike and sample isotopes will behave in an identical fashion, both chemically and in the ion source of the mass spectrometer.

Coal and fly ash analysis by this method depends upon sample dissolution. Unfortunately, the acids required to completely dissolve these materials (HF, $HClO_4$, H_2SO_4) are difficult to obtain in a pure form and also produce undesirable molecular ion species in the spark source. High pressure dissolution in a teflon lined pressure bomb (Parr Instrument Co.) using HNO_3 and HCl has been tried, but silicate species are usually not soluble under these conditions. Other methods, such as NaOH fusion followed by HCl treatment produced clear solutions, but these contained an unacceptable amount of NaCl which gave rise to mass spectral interferences.

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Because of the difficulty of dissolving these materials, a dry mixture technique was developed,[1-3] which involves the use of a 'spiked' matrix material such as high purity Ag or graphite. Separated isotopes of the elements of interest were dried from solution onto the matrix and vigorous shaking in a ball mill ensured homogeneity. This spiked matrix was analyzed alone in order to determine the blank levels and was then mixed with standards (NBS SRM 1632 Coal or 1633 Fly Ash) to determine the amount of each isotope added. This standardization also provided any relative sensitivity corrections which were necessary in this technique.

Table I shows the composition of a spiked Ag matrix (99.9999% pure Ag Cominco American, Inc.) which was used in the analysis of coal (after ashing at 500°C in air to remove the organics) as well as fly ash. The isotopes chosen were usually minor ones in nature which were highly enriched and chosen to be free of spectral interference.

The instrumental operating parameters are summarized below:

Instrument:	AEI MS-702R with photographic plate detection.
Spark conditions:	30 kV rf; 100 pulses per second, 25 μsec pulse length.
Vacuum:	Source <1 x 10^{-4} torr; analyzer 2 x 10^{-8} torr.
Photoplate:	Ilford Q2 or Kodak SWR.
Development:	3 minutes in conc. D-19.

A photoplate data reduction system was used which utilized a minicomputer interfaced with a microdensitometer.[4] The computer accepts digitized optical transmittance data as the densitometer scans over a line. It then computes peak height corrected for background and converts this into relative (ion) intensity using a stored calibration curve (Churchill two-line calibration method[5]). The relative (ion) intensities are employed in the computer code to obtain elemental concentrations according to the Hintenberger[6] isotope dilution equation.

The concentration of the element being measured is obtained from the following equation.

$$x = y \left(\frac{R_t - R_m}{R_m - R_s}\right) \cdot \frac{A_s}{A_t} \cdot \frac{T}{S} \qquad 1)$$

where x = weight of element in the sample.

y = weight of element in the tracer spike.

R_t = isotope ratio of the spike, $\frac{\text{reference isotope}}{\text{tracer isotope}}$.

R_m = isotope ratio of the mixture, $\frac{\text{reference isotope}}{\text{tracer isotope}}$.

R_s = isotope ratio of the sample, $\frac{\text{reference isotope}}{\text{tracer isotope}}$.

A_s = atomic weight of the sample element.

A_t = atomic weight of the tracer.

T = atom % of the spike isotope in the tracer.

S = atom % of the spike isotope in the sample.

The terms: A_s, A_t, T, S, R_s, R_t, and y are usually known in advance, and since R_m can be very accurately measured, it is not unusual to obtain precision and accuracy on the order of 5% for trace element determinations. After equilibrium between spike isotope and sample reference isotope is obtained, quantitative results are assured by isotope dilution even when a low yielding chemical purification is required.

RESULTS AND DISCUSSIONS

Table II shows results for NBS SRM 1632 using the dry spike technique, with SRM 1633 acting as the standard. The results agree within experimental precision for all elements shown. It was possible to analyze a number of other elements by the same technique, provided the concentration in the standard was known with some certainty. In all, twelve elements are routinely reported in coal by this method with a precision and accuracy of about ±15% RSD.

Any analysis of coal or fly ash by SSMS is subject to mass spectral interference arising from the major elements present. These include Si, Al, Ti, Mg, Fe, Na, K and S. Combinations of these elements, oxides, silicates and chlorides, as well as molecular ions from the matrix element (Ag_2^+, AgO^+) must all be considered for their potential effect on the analysis. Certain elements are generally always interfered with (Co^+ by CaF^+ and Sb^+ by AgO^+), while other isotopes are only occasionally affected. Therefore, if a small number of elements is to be analyzed, the analyst should consider using separation and concentration methods to eliminate possible interferents.

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Table I

Spiked Silver for Coal and Fly Ash Analysis

Element	Isotope	Enrichment	Nominal Concentration
Pb	204	99.7	10 ppm
Tl	203	94.9	5
Ba	135	93.6	50
Te	125	91.2	10
In	113	96.4	5
Cd	111	91.3	5
Mo	97	94.3	5
Sr	86	95.7	100
Se	77	94.4	10
Zn	67	89.7	30
Cu	65	99.7	30
Ni	61	99.5	30
Fe	57	93.6	100
Cr	53	96.4	30
K	41	99.4	200

Table II

Analysis of SRM 1632 Using SRM 1633 as Standard

Element	Conc. in μg/g ± RSD	NBS Certified
Tl	0.6 ± 0.2	0.59 ± 0.03
Pb	33 ± 3	30 ± 9
Cd	0.4 ± 0.2	0.19 ± 0.03
Zn	32 ± 8	37 ± 4
Cu	15 ± 3	18 ± 2
Ni	15 ± 3	15 ± 1
Cr	19 ± 3	20.2 ± 0.5