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Improvement in the analysis of ashes from coal by spark source mass spectrography

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IMPROVEMENT IN THE ANALYSIS OF ASHES FROM COAL BY SPARK SOURCE MASS SPECTROGRAPHY

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Improvement in the analysis of ashes from coal by spark source mass spectrography

by

Tim David Welcomer

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
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DOCTOR OF PHILOSOPHY

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For the Graduate College

Iowa State University
Ames, Iowa

1982

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LIST OF ACRONYMS AND ABBREVIATIONS

AAS	Atomic absorption spectrometry
a.c.	Alternating current
AES	Atomic emission spectroscopy
ASTM	American Society for Testing Materials
ATWT	Atomic weight
av	Average
CO	Colorado
d.c.	Direct current
EP	Electrostatic precipitator
EPA	Environmental Protection Agency
GC-MES	Gas chromatography-microwave emission spectroscopy
HTA	High-temperature ash
IA	Iowa
INAA	Instrumental neutron activation analysis
IPAA	Instrumental photon activation analysis
log	Logarithm
LTA	Low-temperature ash
m/z	Mass-to-charge ratio
NBS	National Bureau of Standards
nC	Nanocoulomb
PDC	Primary dust collector
PGAA	Neutron-capture prompt gamma-ray activation analysis
ppb	Parts-per-billion

ppm	Parts-per-million
ppma	Parts-per-million atomic
ppmw	Parts-per-million by weight
psi	Pounds-per-square-inch
rel.	Relative
r.f.	Radio-frequency
RSC	Relative sensitivity coefficient
r.s.d.	Relative standard deviation
SRM	Standard reference material
SSMS	Spark source mass spectrography
std.	Standard
WC	Whole coal
XRF	X-ray fluorescence spectrometry

I. INTRODUCTION

Our highly technological society demands increasing amounts of energy to maintain its high standard of living. However, our national security is threatened by our dependence on imported oil. Also, the question of whether the benefits of nuclear energy outweigh the dangers is still unanswered. The most abundant fossil fuel resource in the United States is coal, but its increasing use also presents problems. The burning of coal creates a large amount of waste in the form of ash. The manner of disposal of this ash is important because it contains many elements which could adversely affect the environment and human health (1-5). Improper disposal could lead to hazardous amounts of many elements in the soil and water.

The periodic table in Fig. I-1 shows the elements of concern (6). Low levels of arsenic, cadmium, mercury and lead are toxic to most biological systems (6). The increased salinity of the soil (7-9), boron (9,10) and, to a lesser extent, copper, nickel and zinc (6) are all toxic to crops (11) and other plants. Molybdenum and selenium (12-14), and, to a lesser extent, chromium, vanadium and fluorine (6) are toxic to livestock at elevated levels, and ultimately hazardous to human health (6,15). Uranium and thorium are concentrated in the ashes and the increased radioactivity could be deleterious; however, more study of this problem is needed (6,15). Inhalable gases and submicrometer particulates can also provide a pathway for toxic elements to enter biological systems. The oxides of sulfur and nitrogen produce hazardous "acid rain".

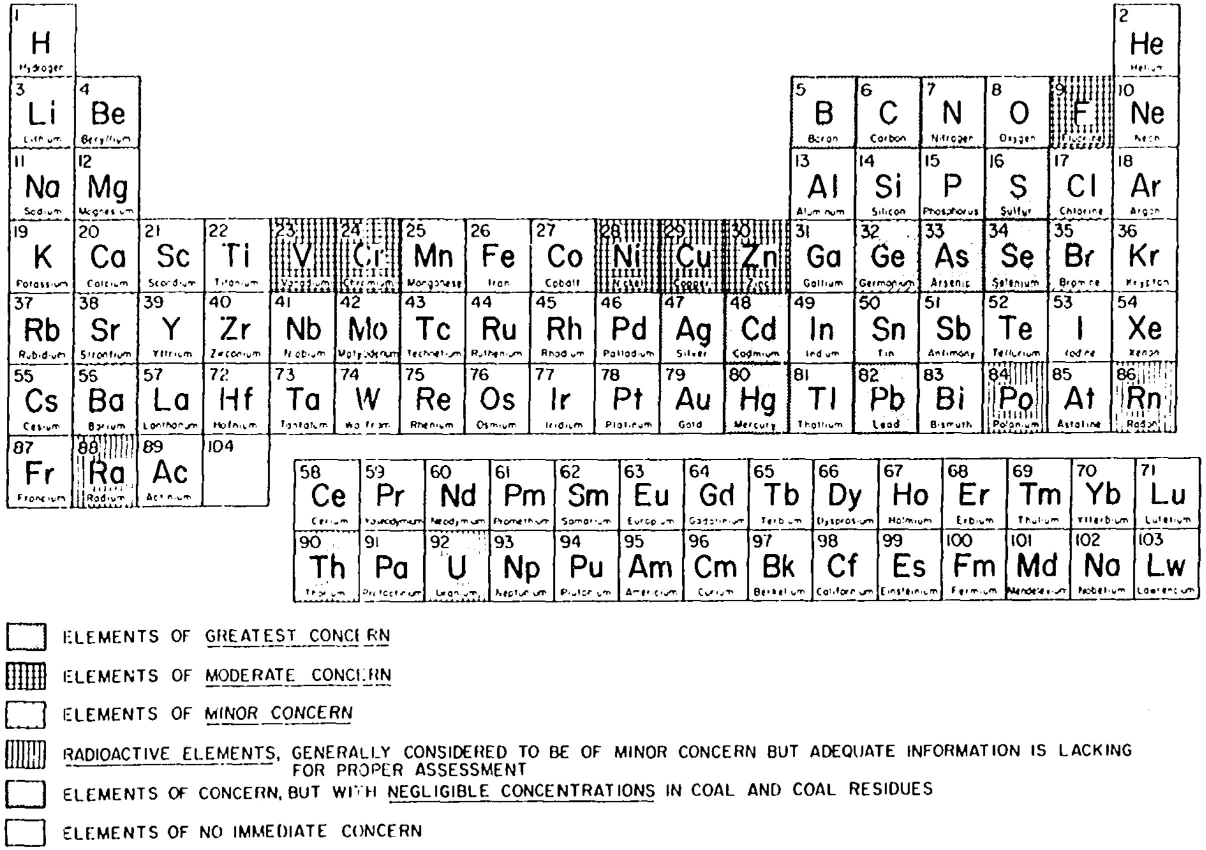

Figure I-1. Periodic table

Particulates highly concentrated in many of the toxic elements enter the body through the respiratory tract (1,5,16-18).

The waste ash can also be useful. Under controlled conditions, the ash can be added to the soil to provide nutrients to aid the growth of useful crops and other plants (10,19-21). Acidic soils and acid mine drainage can be neutralized by the addition of proper amounts of ash (10,22). The ash has a high adsorption capacity and can be used to remove hazardous and unpleasant elements and organic species from surface and waste waters (22). The ash can also be used as a conditioner for industrial waste sludge (22). The ash is used extensively in construction and soil stabilization (23). Another use being developed is the extraction of minerals from the ash (23). Two of the most important minerals are ferric oxide (24,25) and alumina (26,27). The ash may also be a source of metals for which good ores are scarce.

To determine the potential environmental and potential commercial impact of the combustion of a certain coal and the disposal of its ash, a materials balance study of the fluent coal and the effluent ash needs to be performed. The analytical method used should have several demanding characteristics. The number of potentially hazardous and useful elements is large, so the method should be capable of multielement analysis. The elements of interest range in concentration from ultratrace to major constituents, so the method should be sensitive with low detection limits and have a high linearity of response over the concentration range. The method must be economically feasible with a low cost x time/element ratio. The analytical method of spark source mass spectrography is capable of meeting these requirements. All of the elements from lithium to uranium can be recorded simultaneously and permanently on a photographic plate (28-31). The detection limits for the elements range from 100 to 1 ppb (29,30). The linearity of response and dynamic range of concentration of the photographic emulsion are of the order of 10^5 to 10^7 depending on the number of exposure levels used (29,31). The cost and amount of time for an analysis are relatively high, but the number of elements analyzed is relatively very large, so on a cost per element basis, it is an economically feasible method when compared to other possible analytical methods.

The major disadvantage of this method is the sensitivity of analytical accuracy and precision to a number of factors. These factors include the homogeneity of the sample, the stability of the radio frequency (r.f.) spark, the matrix of the sample, the complexity of the mass spectrum, and the calibration of the photographic emulsion. These factors are particularly important in the analysis of ash from coal. In a typical analysis, less than 10 mg of sample is consumed. Great care must be taken to assure the maximum homogeneity of the sample (29,32), especially for ash which is a very inhomogeneous substance. An erratic r.f. spark is detrimental to the analytical accuracy and precision (33), so the spark should be stabilized as much as possible. The ionization efficiency of the spark is dependent upon the sample matrix (34). Good standard samples with matrices similar to that of the ash are needed to calculate accurate relative sensitivity coefficients for the elements (35). The ash contains most of the elements in the earth's crust which results in a very complex mass spectrum. This complexity limits the number of choices of elements to be used as internal standards because of spectral interferences (36). The accuracy of the analysis is also dependent upon the accuracy of the calibration of the photographic emulsion (37-39).

The purpose of this research was to develop a method of analysis for ash from coal by spark source mass spectrography which would assure good homogeneity of the sample, improve the stability of the r.f. spark, determine accurate relative sensitivity coefficients for the elements in the ash matrix, select internal standards free from spectral interferences, and provide an accurate calibration of the photoplate emulsion. The effectiveness of this method was to be tested by the performance of a mass balance study on the coal burned at the Iowa State University power plant.

II. PRINCIPLES OF SPARK SOURCE MASS SPECTROMETRY

A. Ion Source

Ions are formed in spark source mass spectrometry (SSMS) when a radio frequency high voltage is applied between two conducting sample electrodes. The resulting sparks volatilize a small amount of the sample and create ions of its constituent elements. Electrodes of conducting samples can be in the form of rods, bars, chips, needles, or any other tractable form. Nonconducting samples must be powered, mixed with a spectroscopically pure conducting powder (graphite, silver, etc.), and compressed into suitable electrodes. The sparking process takes place at a pressure $\leq 10^{-5}$ torr in a special differentially pumped vacuum housing.

Sample electrodes are mounted in appropriate holders which can be manipulated from outside the vacuum housing. The electrodes are surrounded by a special shield which is maintained along with the electrodes at the ion accelerating d.c. potential of 15-30 keV. The purpose of the shield is to maintain a uniform electric field around the electrodes, to reduce contamination of the source housing by materials sputtered from the electrodes, and to prevent overloading the accelerating voltage power supply (33). The shield also serves to minimize the need to clean the housing periodically and reduces the instrument "memory" from one sample to the next.

A pulsed 1 MHz potential of $\sim$ 100 kV, peak-to-peak, is applied between the sample electrodes. A schematic view of the circuit is shown in Fig. II-1. Spark parameters can be varied as required. Pulse lengths between 20 and 200 μs are available and pulse repetition rates can be varied from one to several thousand pulses s^{-1}. The r.f. spark consists of a number of consecutive distinct voltage breakdowns during each pulse (40). This number depends upon the electrode gap width which in turn determines the breakdown voltage and the relaxation time of the r.f. voltage in the spark circuit. Successive breakdowns characteristically occur several r.f. cycles after a previous breakdown.

The r.f. spark is a very energetic chemical environment. Sample material is volatilized and ions are formed from the surface of the electrodes in a pulsating plasma rich in ions and electrons. The kinetic energies of the ions can be several hundred to several thousand keV. These ions are accelerated into the grounded mass spectrometer with energies corresponding to the accelerating voltage.

B. Electrostatic and Magnetic Analyzers

The large energy spread of the ions formed by the r.f. spark necessitates the use of a mass spectrometer with very good focusing and resolving capabilities. The majority of spark source instruments are double-focusing using the Mattauch-Herzog geometry. A diagram of a typical instrument is shown in Fig. II-2 (41).

The coupling of an electrostatic field with a magnetic field in tandem provides both velocity and directional focusing, plus mass dispersion. The electrostatic field produces an energy spectrum by dispersing the narrow ion bean (42) according to:

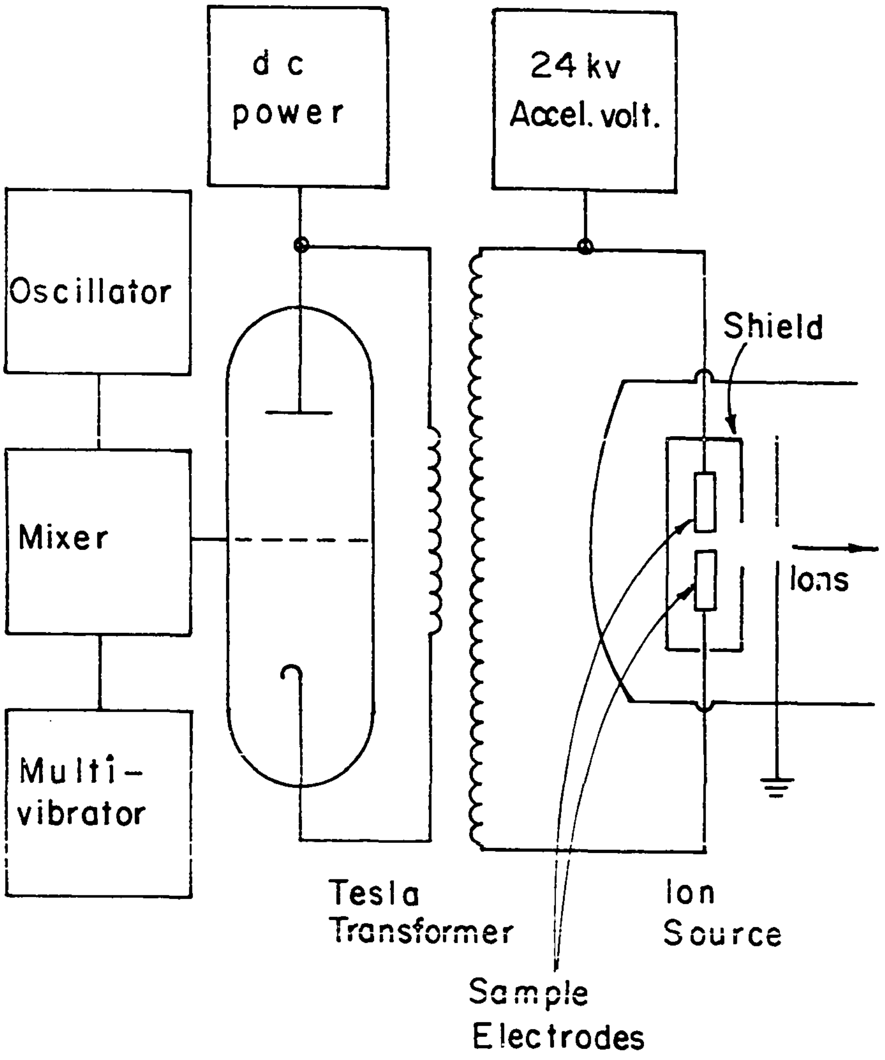

Figure II-1. Radio-frequency spark circuit

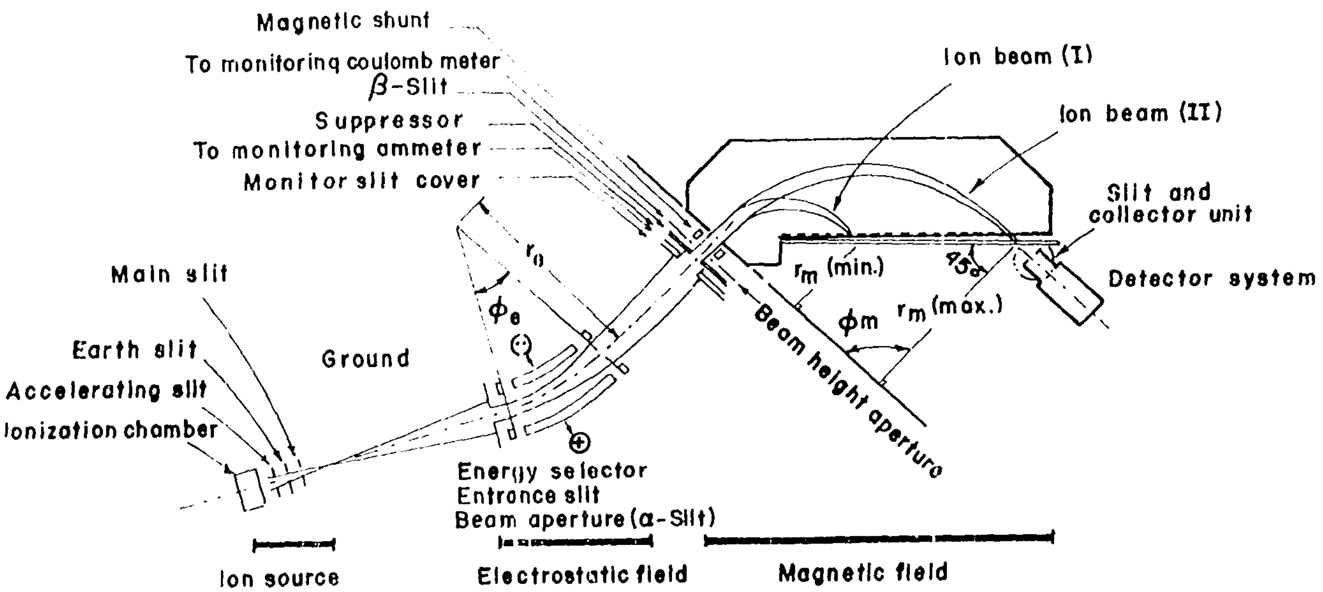

Figure II-2. Spark source mass spectrograph with Mattauch-Herzog geometry

$$D_e = \frac{\Delta r_e}{2} [(1 - \cos \sqrt{2}\,\phi_e) + \frac{\ell_e'}{r_e} \sqrt{2} \sin \sqrt{2}\,\phi_e] \qquad \text{(II-1)}$$

where r_e is the radius of curvature of the electrostatic field, ℓ_e' is the object distance, and ϕ_e is the deflection angle of the field. Only ions with a certain small energy spread enter the magnetic field which focuses ions of equal m/z, but differing velocities, to a single point. The mass dispersion (42) is described by:

$$D_m = \frac{\Delta r_m}{r_m} [r_m(1 - \cos \phi_m) + \ell_m''(\sin \phi_m + (1 - \cos \phi_m)\tan e_m'')] \qquad \text{(II-2)}$$

where r_m is the radius of curvature of the magnetic field, ℓ_m'' is the image distance, ϕ_m is the deflection angle of the field, and e_m'' is the angle made by the average ion beam as it exits the field and the perpendicular to the field boundary.

In general, double-focusing is obtained for only one value of r_m, but under certain conditions all the ions can be focused in the same plane. These conditions (41) require that the entrance slit to the electrostatic field must be at the object focus, and the ions must exit the electrostatic field and enter the magnetic field as a parallel beam. The Mattauch-Herzog geometry satisfies these conditions. An ion-sensitive photographic plate can be placed at the exit pole boundary of the magnetic field to record the mass spectrum.

The mass resolution ($R = \frac{M}{\Delta M}$, where M is mass) provided by this instrument geometry depends solely on the constants associated with the electrostatic field (42) according to:

$$R = \frac{r_e}{S'_e} \qquad \text{(II-3)}$$

where S'_e is the entrance slit width. However, the mass dispersion depends solely on the constants associated with the magnetic field according to Equation II-2. The position of a spectral line on the photographic plate is directly proportional to the square root of its m/z. Generally, both analyzers are operated at a pressure $\leq 10^{-8}$ torr.

C. Photographic Detection

Ion-sensitive silver bromide photographic plates are commonly used in SSMS to provide a permanent sensitive record of mass spectra in a small amount of space. The complete mass spectrum from Li to U can be recorded simultaneously. Both major and ultra-trace elemental analyses can be performed in one experiment by recording a sequence of different exposure levels.

The photographic emulsion is a collector-transducer-recorder combined into one system. Sensitivity and the shape of the response curve are the two primary measures of the performance of the emulsion (43). Sensitivity is defined as the fractional area blackened per incident ion density, for vanishingly small ion densities (44). An ion produced by the r.f. spark is energetic enough to make a single halide crystal developable (45). The sensitivity is dependent upon both the mass and energy of an ion. This topic will be discussed in detail in Chapter IV in this dissertation. The reproducibility of an exposure depends on the uniformity of the emulsion on a photoplate and from plate to plate, as well as on the developing process.

The response of the emulsion is expressed as fractional blackening B or transmittance T, where B is directly proportional to the number of blackened halide grains (46)

$$B = 1 - T = (\psi_0 - \psi)/\psi_0 \qquad \text{(II-4)}$$

and where ψ_0 is the light intensity incident on the photoplate, as measured by a microphotometer, and ψ is the light intensity transmitted through the plate. Two parameters are measured to evaluate the response of an emulsion: the total ionic charge Q, as measured by an integrating ion monitor; and B (47). The reciprocity law is valid for these ion-sensitive emulsions (48). Consequently, the emulsion is an integrating detector. The total number of exposed halide grains in a spectral line (*i.e.*, the area under the intensity curve for the line) is directly proportional to the concentration of the ion in the total ion beam for that exposure.

One major phenomenon which limits sensitivity is secondary blackening. Secondary blackening is due to two major causes (47): charge exchange between ions and neutral species producing diffuse bands which occur in predictable regions of the spectrum, and blackened regions, known as "fog" or "halo", near major elemental lines, which are produced by several complex mechanisms (49,50). Several methods have been used to reduce this blackening (51-55). One important method involves a developing process by which the emulsion is first bleached and then allowed to undergo internal development (56). This method can improve the sensitivity by a factor of three (57).

The recorded mass spectra are evaluated by computer methods. The microphotometer which measures the positions and transmissions of the spectral lines produces data which are treated by means of a number of computer programs. These programs determine the exact m/z values for the lines and the ion concentrations. Other programs evaluate the results and the exposure data to determine the elemental concentrations in the sample.

The precision obtainable by this method of analysis is generally about ±20% relative standard deviation (r.s.d.) (29). The accuracy is generally about ±30% r.s.d. Isotope dilution SSMS (28) and recent developments in the use of electrical detection (58) improve both the precision and accuracy to ±3-5% r.s.d.

III. REVIEW OF RELATED WORK

A. Other Methods of Analysis for Coal and Ashes

1. Instrumental neutron activation analysis

The multielemental method for analysis used most often for coal and ash is instrumental neutron activation analysis (INAA) using thermal neutrons. INAA is a nondestructive technique potentially capable of simultaneous multielement detection. The time of analysis per sample can be small because many samples can be irradiated at once. This method is especially good for the assay of minor and trace elements in coal because the major constituents of coal, carbon, oxygen and hydrogen, are not activated by thermal neutrons. The normal procedure used in INAA is to dry the samples and place them in polyethylene vials for short irradiation periods, or quartz vials for longer ones. Standard samples are treated in like manner. The vials are placed in the core of a nuclear reactor and irradiated by thermal neutrons. The vials are removed and the gamma-ray spectra of the samples and standards are counted and energy analyzed at a fixed geometry using a Ge(Li) detector. The counting data are processed by computer and the analytical results are reported. Every isotope has a unique half-life and gamma-ray emission energy. The intensity of the emission of an element is proportional to its concentration.

Many analyses have been performed on NBS coal and ash standards to demonstrate the applicability of INAA to the analysis of these types of samples (59-74). Differences in matrix between samples and standards are not important because only the nuclear properties of the elements are involved in the analyses (60). The coincidence of gamma-rays emitted by certain elements and their measurement by dual detectors has been used to improve the sensitivity of the method for some elements (65). The level of the thermal neutron flux (68) and the energy of the impinging neutrons can be selected to improve the analytical results for certain elements (71). The precision and accuracy of the method is generally ±10% or better for most elements. As many as 42 elements have been detected simultaneously in standard samples (72). Coal and ash samples from power plants have been analyzed by this method (5,75-82) using NBS standards and samples from other sources as standards. As many as 44 elements in real samples have been analyzed successfully with elemental precisions and accuracies ranging from ±5-20% (78).

Radiochemical separations are performed when spectral interferences occur. The irradiated samples are dissolved and the elements of interest are separated from interferences by chromatographic (83-89), distillation (90,91), or other suitable methods (92-95).

Irradiation with epithermal neutrons improves the sensitivity of the method for a number of elements (96-101). Irradiation with both thermal and epithermal neutrons can improve the analytical results for up to 44 elements in power plant and standard samples (97,102,103).

2. Neutron-capture prompt gamma-ray activation analysis

Neutron-capture prompt gamma-ray activation analysis (PGAA) is a technique very similar to INAA. The method of sample preparation and irradiation is the same, but the gamma-rays emitted immediately after neutron-capture are detected. The emission of some elements which do not yield convenient radioisotopes for detection by INAA can be measured. Most of the analyses performed by PGAA have concerned NBS and Illinois State Geological Survey coal and ash standard samples (74,104-107). As many as 17 elements have been analyzed simultaneously with precisions and accuracies as good as or better than ±10% (74,107).

3. Instrumental photon activation analysis

Instrumental photon activation analysis (IPAA) is a technique also very similar to INAA. The samples are irradiated with high energy electrons (MeV range) instead of neutrons. The electron energies are selected to yield the best sensitivities for the elements of interest. The gamma-ray emission is detected in the same manner as in INAA. Most of the analyses performed by IPAA have concerned NBS coal and ash standard samples (62,72,93,108-110). As many as 36 elements have been analyzed simultaneously with precisions and accuracies as good as or better than ±10% (72). IPAA is often used in conjunction with INAA to provide the best sensitivity possible for each element of interest by judicious selection (62,72,93).

4. X-ray fluorescence spectrometry

X-ray fluorescence spectrometry (XRF) is also a nondestructive, sensitive, multielemental method of analysis for coal and ash samples. An advantage of XRF over INAA is that a nuclear reactor is not needed. Samples are commonly prepared by homogeneous mixing with a pure, self-binding support material which has a noninterfering XRF spectrum. The mixture is pressed to form a thin disk and placed in the spectrometer. An x-ray tube and interchangeable secondary targets (*e.g.*, Zr, Mo, Tb, Ag) are used to produce nearly monochromatic excitation radiation for each group of elements of interest. The fluorescence is detected using a Si(Li) detector. Energy-dispersive XRF permits simultaneous detection of all radiations. The spectrometer is calibrated by using standard samples. A variety of methods are used to correct for matrix effects and background radiation.

Many analyses have been performed on NBS standard coal and ash samples (4,79,82,111-115) to demonstrate the applicability of this method to the analysis of these types of samples. As many as 40 elements have been detected simultaneously in these standard samples with precisions and accuracies better than ±10% (112). Coal and ash samples collected from power plants have been analyzed (4,79,91,115,116) using NBS standards and samples from other sources as standards. As many as 29 elements in real samples have been analyzed successfully with precisions and accuracies ranging from ±5-10% (115).

5. Atomic emission spectroscopy

Atomic emission spectroscopy (AES) has been used extensively for the analysis of coal and ash samples. The instrument has an excitation source, of which there are several different types, a monochromator for single elemental analysis or a polychromator for multielemental analysis, and a detector, usually either a photographic plate or film (spectrography), or a photomultiplier tube or tubes (spectrometry). The photographic method of detection requires the calibration of the emulsion. A rotating stepped sector disk is used to record different exposure levels and the step ratio determines the manner in which the emulsion is calibrated. The internal standard method of analysis is generally used with photographic detection. A spectrometer is calibrated with standard solutions. The types of samples to be analyzed and the elements of interest determine the type of excitation source used.

In the past, the excitation source used most often for the analysis of coal and ash samples has been the d.c. arc (91,117-124). The analyses have generally been multielemental using photographic detection (118-122, 124). The powdered sample is homogeneously mixed with the internal standard and placed in the cup of a graphite sample electrode. The sample is excited by the d.c. arc produced between sample and counter electrodes. As many as 36 elements have been detected in 900 ashed coal samples (121) and the precision and accuracy of the method is usually better than ±15% (91,117,119,123,124). The a.c. arc (125) and spark (124) excitation sources have also been used to analyze these types of samples.

The inductively coupled plasma excitation source requires dissolution of the sample. The sample solution is injected into a radio frequency excited, inductively coupled argon plasma. The atomic emission of the sample constituents is diffracted by a grating in a polychromator and the spectrum is detected simultaneously by a series of photomultipliers. Also, a computer controlled scanning monochromator, which can increase the number of elements detected, can be used in place of the polychromator arrangement (126,127). Fusion dissolution methods have been the most successful for coal and ash analysis by this technique (61,127). As many as 28 elements have been detected in NBS standard and power plant coal and ash samples with precisions and accuracies as good as ±3% (61).

Gas chromatography-microwave emission spectroscopy (GC-MES) is an AES technique which is normally used for the single elemental detection of certain volatile metalloids in coal and ash samples (79,128,129). The samples are dissolved and the elements of interest are complexed selectively by organic chelates. The sample is injected into a GC and the separated elements enter a quartz tube containing an argon microwave plasma. The emission enters a monochromator and elemental detection is achieved using a photomultiplier tube. Arsenic (129) and selenium (79, 128) have been detected in NBS and power plant samples with precisions and accuracies better than ±5%. Other excitation sources which have been used for single elemental analysis of these samples are the radio frequency (r.f.) furnace (130) and the helium glow discharge (131).

6. Atomic absorption spectrometry

Atomic absorption spectrometry (AAS) has been used extensively for the analysis of individual elements in coal and ash samples. The spectrometer has a source of absorption radiation (*e.g.*, hollow cathode lamp, electrodeless discharge lamp), a means of atomizing the sample, of which there are several, a monochromator, and a detector, usually a photomultiplier tube. The spectrometer is calibrated with standard solutions. The source lamp must be changed for each element of interest and the instrument recalibrated. The types of samples to be analyzed and the elements of interest determine the type of sample atomization used.

Sample atomization by flame is a method commonly used for the analysis of coal and ash samples (4,5,31,82,91,132-137). The flame is produced by the ignition of a mixture of an organic gas and oxidizer gas (e.g., acetylene-air, acetylene-oxygen). The sample is dissolved and aspirated into the flame absorption cell of the spectrometer. The flame atomizes the sample and the absorption of the element of interest is measured. A variety of fusion and acid dissolution methods have been used for coal and ash samples. As many as 17 elements in NBS and power plant ash samples (137) and 8 elements in NBS and power plant coal samples (31) have been detected with precisions and accuracies better than ±5%.

Sample atomization by a graphite furnace can improve the sensitivity of the method for many elements (31,80,91,134,135,137-143). The furnace is a hollow graphite cylinder electrically connected to a low voltage high current supply. Several microliters of sample solution are injected into the furnace through a small hole in the cylinder. The power supply is programmed to first dry the sample, then ash any residue, and finally atomize the sample. The absorption signal is measured by a photomultiplier tube. This technique is rapid; the time of analysis can be as little as 30 seconds. Eleven elements in NBS standard fly ash (134) and six elements in power plant coal samples (31) have been detected with precisions and accuracies similar to the flame technique. Analyses using a silica furnace (144) and a r.f. furnace (130) have also been performed. A direct method of analysis for lead in ash has been developed using this technique (145). The sample is ground and mixed with pure graphite powder and placed in a graphite cup. The cup is heated to a temperature which volatilizes and atomizes the lead, but not the matrix.

Mercury, a highly volatile element, is easily lost during sample preparation. A large number of flameless methods of sample atomization have been developed to counteract this problem (4,61,77,79,80,146-151). Most of these methods use a digestion (146-148) or combustion (149,150) technique to release the mercury from the sample. Then the mercury is either adsorbed on an appropriate support and atomized in a furnace absorption cell (146,149,150), or transported to an unheated absorption cell by an appropriate carrier gas (61,80,147,148,151). The precision and accuracy attained by most of these methods have been better than ±10%.

A number of other spectroscopic methods of analysis for individual elements in coal and ash samples have been developed. Colorimetric methods have been used for the analysis of arsenic (152-156), mercury (77,157), zinc (158), boron (80), lead (159), and beryllium (160). Fluorimetric methods have been used for the analysis of selenium (80) and uranium (161-163). Precisions and accuracies are generally as good as or better than ±10%.

7. Specific ion electrodes

Specific ion electrodes have also been used for the analysis of individual elements in coal and ash samples. The sample is dissolved and an appropriate ionic strength buffer added to the solution. The specific ion activity is measured by the ion-selective electrode for the element of interest *versus* a saturated calomel reference electrode. The concentration of the element is determined by the method of standard additions or calibration with standard solutions. The halogens are the elements most often analyzed by this method. Fluorine (61,91,164) and chlorine (61) concentrations in NBS coal and power plant coal and ash samples have been determined with precisions and accuracies as good as ±2% (61).

8. Anodic stripping voltammetry

Anodic stripping voltammetry is another electrochemical method which has been used for the analysis of individual elements in coal and ash samples. The sample is dissolved and the solution conditions adjusted to allow for the electroanalysis of the element of interest. Inert analytical and counter electrodes are placed in the solution along with a saturated calomel reference electrode. A potential is applied to the electrolytic cell which will cause electrodeposition of the analyte onto the surface of the analytical electrode. The potential is then scanned to a value which completely strips the analyte from the electrode surface. The resulting current (I) *versus* potential (E) curve is recorded. The area under this curve is proportional to the concentration of the analyte. Concentrations are commonly determined using the method of standard additions. Cadmium, lead, and zinc have been detected in power plant fly ash samples (80) and selenium has been detected in NBS standard coal and fly ash samples (165).

Other types of analytical methods which have been used for the analysis of individual elements in coal and ash samples are titrimetric (166-168) and gravimetric (169).

B. Accuracy of the Analysis of Samples Related to Coal and Geological Materials by Spark Source Mass Spectrography

There are a number of advantages to performing the analysis of coal and other types of geological materials by spark source mass spectrography (SSMS) (36). The technique is multielemental, simultaneously detecting more elements than INAA (170). SSMS is highly sensitive with detection limits for the elements in geological matrices ranging from 5-20 ppb by weight (36,171). Also, SSMS does not exhibit order of magnitude variations in sensitivity for different elements in the same matrix like INAA and AAS (172). Only a small amount of sample is needed for an analysis, a minimum of about 10 mg, and the time of analysis per element detected is low (36).

There are a number of factors which determine the precision and accuracy of an analysis by SSMS. The homogeneity of the sample electrodes is important (28,173-177). Care must be taken not only to insure the homogeneity of the sample and sample-graphite mixture, but also the homogeneity of the internal standard in the electrodes if the doping method is used (172,178). Homogenizing methods vary from simple grinding and thorough mixing to complex methods of dilution by multiple fusion (35,188). The error due to sample electrode inhomogeneity can be less than 5% (35,36,174). The shape of the sample electrodes should be consistent (28,38,179,180). The spark parameters (e.g., repetition rate, pulse length) and spark gap width should be constant (28,35,38,171,173, 178,177,179-183). These parameters affect the relative elemental ionization efficiency in the spark and the ion charge distribution in the spark plasma (31,173,178,183). Generally, changes in the gap width have a greater effect than does pulse repetition rate and pulse length (177). Use of the ion intensity ratio of the analyte and internal standard from the same exposure in determining elemental concentrations can minimize the effect of spark variations (36). The effect of changes in the gap width and ion charge distribution can be minimized by stabilizing the intensities of the matrix lines (184). The positioning of the spark with respect to the entrance slit should be consistent (28,177). The spark position determines what portion of the inhomogeneous spark plasma is sampled by the mass spectrograph (38, 175-177,179,180). Other factors concern variations in the ion current at the monitor (177,185) and the spark discharge with time caused by circuitry instability, aging, and other time related variations (171, 184). Also, the vacuum in the ion source should be consistent (28).

The photoplate should be properly aligned in the focal plane of the spectrograph, otherwise there could be a loss of resolution (186, 187). The photoplate emulsion should be consistent across the plate and between plates (28,36,171,173,177). The inhomogeneity of the emulsion limits the analytical precision to 3-5% (36,173,177). A reproducible procedure for the developing of the photoplates should be used (28). Another factor is the variation in the microphotometer line transmittance values (31,175,177). The spectral line width is dependent on the ion path length in the magnetic analyzer and is directly proportional to the square root of the m/z ratio. A correction in the calculation of ion intensities should be made for this phenomenon if only peak heights are measured (28,31,36,175,180,185,189,190). Errors caused by line width, space-charge broadening, and other variations in line shape can be minimized by using line area in the calculation of ion intensity (173,175,180,186,187). The line transmittances should also be corrected for background (28,31,175,190). The sensitivity is limited for low mass ions and the +2 ions of the transition metals by the background fog caused by the sample matrix and the graphite in the electrodes (191). A number of methods of correction for errors caused by spectral interferences have been devised (36,172,175,177,178,185,189,192). The sensitivity of the photographic emulsion is also dependent on the mass and energy of the impinging ions (31,36,173,175). A number of equations have been derived from experimental observations to correct for this emulsion dependence (28). This characteristic of the emulsion is discussed more thoroughly in Chapter IV of this dissertation.

The choice of the internal standard can affect the precision and accuracy (172,175,178,185,190). A number of criteria for the selection of internal standards have been published (172,175,178,190). The accuracy of the determination of the relative sensitivity of this method for elements in a certain sample matrix affects the precision and accuracy of the analysis (28,31,34-36,38,171-178,180-182,185,188-190, 192-196). The relative elemental sensitivity is dependent on the elemental ionization potential (36,38,172,175,176,180,185,189,192), volatility (35,36,38,172,175,176,180,182,185,189,192), and ionization cross-section, which is determined by the atomic covalent radius (172, 175,181,194). The measure of elemental volatility normally used is the boiling point (36), but melting point (182), heat of sublimation (185, 205), and vapor pressure (187) have also been used. Thermal ionization caused by overheating the electrodes can cause variable elemental sensitivity (35,172). The electrodes can overheat if the spark parameters are not carefully controlled, but this effect can be minimized by cooling the electrodes (182). The elemental volatility has a greater effect on the relative sensitivity than the ionization potential (36, 172,178,182). The method is most sensitive to volatile elements with low ionization potentials (*e.g.*, the alkali metals), which are most subject to problems with thermal ionization. The method is less sensitive to volatile elements with high ionization potentials (*e.g.*, antimony, thallium, lead) and least sensitive to involatile elements (*e.g.*, iridium, zirconium). Some researchers believe that the ionization cross-section has a greater effect on the relative elemental sensitivity than the other parameters (194). The relative elemental sensitivities have been determined by the use of empirical equations derived from these sensitivity parameters (185,197,205). However, these empirical values can be in error by as much as 40-50% (196). Another method of determining the relative elemental sensitivities is by the analysis of standard samples (36,171,172,174,175,177,185,190,192,195, 196,198-204). The sensitivities are determined by comparison of the experimental values with the "true" values determined by independent methods. The accuracy of this method is limited by the accuracy of the independent determinations. The accuracy can be better than ±10% if the spectra of both the unknown and standard sample are recorded on the same photoplate (195). If good standard samples are not available, synthetic standards can be prepared (35,178,189,192). Pure materials are mixed to simulate the sample matrix and this mixture is doped with the elements of interest. The final mixture is then thoroughly homogenized. Some researchers report that the relative sensitivities are not dependent on the sample matrix (36,178), but other researchers do report a matrix dependence (34,35,177,193).

Coal, ash, and other types of geological materials have been analyzed semiquantitatively by SSMS (198,200,206-210). Corrections for relative elemental sensitivities are not used in semiquantitative analysis. The analytical results are usually within a factor of three of the actual values. These materials have also been analyzed quantitatively by SSMS using methods of correcting for the relative sensitivities. The sample is often doped with an internal standard. The internal standard is usually an element which has a concentration in the sample below the detection limit of SSMS for that element. The relative elemental sensitivities are normalized in reference to the standard. Empirical corrections for relative sensitivity have been used in the analysis of these materials (185). Corrections based on the results of the analysis of well-characterized standard samples (36,171, 172,175,188,190,199) and synthetic standards (35,178,189) have also been used. The internal standard can also be an element already present in the sample matrix. The analytical results obtained using this method of selection of the internal standard can be just as accurate as those results obtained by use of the doping method (190). Most of the analyses of these materials using the undoped method have used corrections for sensitivity based on the analysis of standard samples (192,199,202,203). Other analyses of such materials have been performed (18,31,211,212). The quantitative results have an average accuracy of ±30% or better, but the average accuracy can be as good as ±10% for as many as 15-20 elements (188). More than sixty elements can be determined quantitatively in one analysis (190). If fewer than twenty elements are of interest (30), isotope dilution SSMS can be used to improve the average analytical accuracy to a value less than ±10% (172). Other analyses of these materials have been performed by isotope dilution SSMS (174,197,213).

IV. IMPROVEMENTS IN THE ANALYTICAL METHOD OF SSMS

A. Time of Analysis

The time of analysis per sample should be short enough to minimize spectral aberrations caused by instrumental instability. Another advantage of a short time of analysis is rapid data acquisition. However, the time of analysis should be long enough to allow for the detection of the ultra-trace elements in a sample. The time of analysis can be shortened by increasing the ion current to the maximum level before which spectral aberrations caused by space-charge broadening and overheating the sample electrodes become a problem. A rectangular aperture, 0.51 x 1.5 mm, was chosen for the anode plate. This increased the ion current to a level greater than that obtained with a circular aperture and also minimized the buildup of sample on the ion beam collimating slits. This buildup can contribute to instrumental memory. A notch, which fits over a peg in the ion source, was cut into the anode plate to provide for the rapid and reproducible alignment of the plate in the optical path of the spectrograph. The spark parameters and greatest exposure level to be used in the analysis of the ash and ashed coal samples collected for the research project were determined by a series of experiments. The repetition rate and pulse length of the spark, and the amount of charge put on the photoplate were varied. The amount of time needed to complete the exposure was measured. The sample sparked in these experiments was a fly ash collected from an electrostatic precipitator hopper at the Iowa State University Power Plant.

The experimental results are reported in Table IV-1. A time duration for the longest exposure of no more than 30 minutes was desired. An exposure level of 450 nanocoulombs (nC) for the longest exposure and a repetition rate-pulse length of 100 s^{-1} - 3.2 μs were chosen because 450 nC was great enough to allow for the detection of the ultra-trace elements and 100 s^{-1} - 3.2 μs provided reproducible sparking conditions with minimal spark aberrations and sample overheating (187). Together these choices met the 30 minute time duration requirement.

Table IV-1. Time of analysis experiments

Repetition Rate (sec^{-1}) - Pulse Length (μsec)	Exposure Level (nC)	Time Duration (min)
100 - 3.2	600	36
	200	12
	70	4
	20	1.2
	300	20
	100	6
	30	2
	10	0.8
32 - 10	400	49
	100	7
	30	2
	10	0.8
32 - 32	500	32
	200	12
	70	5
	20	1.2

Four sample spectra were exposed on each photoplate to minimize the cost of the project due to the photoplates, but still allow room for a sufficient number of exposure levels to cover the desired elemental concentration range in the samples. Seven exposures per sample fit on the photoplate. The seven exposure levels initially chosen, represented by the charge on a precision capacitor, were 450, 150, 30, 10, 3, 0.3, and 0.03 nC. However, the actual exposure levels recorded on the same basis when the samples collected for this project were analyzed were 450, 150, 30, 10, 15, 1.5, and 0.15 nC. The changes for the three shortest exposures are due to stray capacitances in the monitoring circuitry that were not discovered until after all of the samples were analyzed. These exposure levels provided a total time of analysis per sample of approximately 45 minutes.

B. Sparking of the Sample

A high electrical contact resistance between the graphite-ash sample electrodes and the sample holders can cause spark instability. In some cases, sparking has even been observed between the metal sample holders and sample electrodes instead of between just the sample electrodes (187). A method of reducing this contact resistance was developed. The graphite-ash sample mixture was compressed in a polyethylene mold around a 0.5 mm diameter pure silver wire. The pressure applied to the mold by a hydraulic press was 40,000 psi for a period of 45 seconds. The wire supported the sample with approximately 5 mm of wire left exposed to be gripped by the sample holders. A diagram of the mold and wire is shown in Fig. IV-1. The resistance between the sample holder and electrode was reduced greatly. The wire directed the current through the sample and sparking was observed only between the graphite-ash electrodes. Another advantage of the wire sample support (214) was the greatly reduced chance of breaking the brittle compacted graphite electrodes when being gripped by the sample holders.

C. Calibration of the Photographic Emulsion

The calibration of the photographic emulsion is an important step in the SSMS analytical procedure. Any error in the calibration will adversely affect the accuracy of the analytical results (36,194). The calibration curve is a plot of the transmittance of a mass spectral line *versus* the logarithm (log) of the ion intensity. Historically, the first methods of calibration were graphical. The "many isotope method" uses the measured transmittances of the isotopic lines from elements which have several stable isotopes (*e.g.*, Cd, Sn, Os, Hg) plotted *versus* the log (isotopic abundance) to construct the calibration curve (215). A modified "many isotope method" has been developed which increases the number of elements available for the construction of the curve (178). The Churchill Two-line method uses the transmittance ratios of only two isotopic lines from a single element, but many pairs from different exposures, to construct a preliminary curve (216). The line transmittances of the more abundant isotope are plotted *versus* the line transmittances of the less abundant isotope. The points on the preliminary curve are used to construct the calibration curve. These

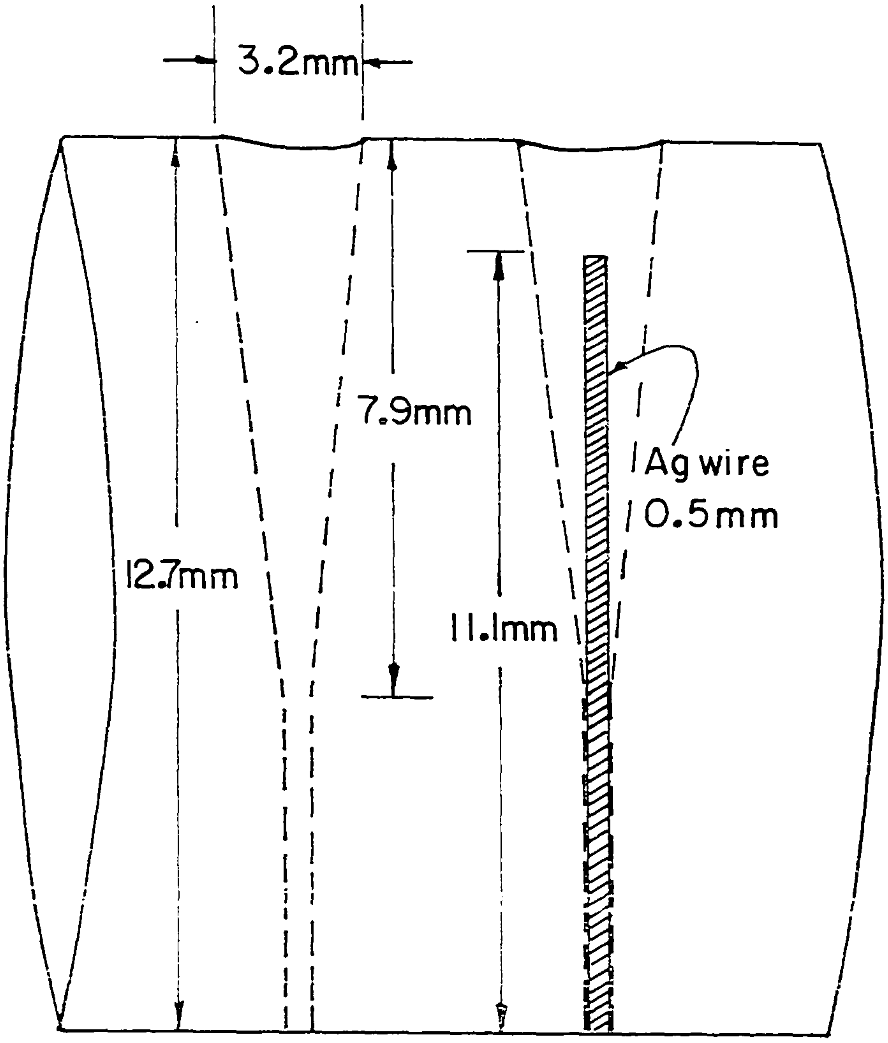

Figure IV-1. Polyethylene mold and Ag wire support line transmittance points are plotted versus the log (isotopic abundance ratio), which is a measure of the log (ion intensity). Only elements which have isotopic pairs with the ratio of their abundances in the 1.2 to 3 range can be used (38,217). This method of calibration has been used in the analysis of coal and ash samples by SSMS (197,212) besides in other work (176,178,183,218-220).

The calibration curve of transmittance versus log (ion intensity) has a limited linear portion (38). A number of methods have been developed to extend the linear portion. The Seidel transformation (221) extends the linear portion by plotting the lot (1/T - 1), where T is the line transmittance, versus log (ion intensity) to construct the calibration curve. The extension of the linear portion increases the useful working range of the curve (36,185,189,192,220,222). The McCrea transformation (223) extends the linear portion by plotting the "reduced transmission", defined as $T' = (T_\ell - T_s)/(T_b - T_s)$, where T_ℓ is the line transmittance, T_s is the saturation transmittance, and T_b is the background transmittance, versus the log (ion intensity). The Wagner transformation (224) extends the linear portion into the high transmittance range (i.e., for faint lines). The log[log(1/T)] is plotted versus the log (ion intensity) to construct the calibration curve.

Mathematical formulae have been derived to describe the calibration curve. These formulae are especially useful for computer application (38). The Hull equation (225) is derived empirically. It takes the form:

$$\log\ (\text{ion intensity}) = \frac{1}{R} \log \left(\frac{1 - T_\ell}{T_\ell - T_s}\right) - \log k \qquad \text{(IV-1)}$$

or

$$T_\ell = T_s + \frac{1 - T_s}{1 + [k(\text{ion intensity})]^R} \qquad \text{(IV-2)}$$

where T_ℓ is line transmittance and T_s is saturation transmittance. The parameter R is a measure of the slope of the curve and the constant k is a measure of the sensitivity of the emulsion. The parameters R and T_s permit a least-squares fit of the formula to experimental transmittance values. The Hull equation has been shown to be quite useful in SSMS work (198,226-230) and an improvement over other methods of calibration (231,232). The Kinoshita equation (233) is derived theoretically. It takes the form:

$$T_\ell = 1 - [1 - T_s(1 - e^{-q(\text{ion intensity})})] \qquad \text{(IV-3)}$$

where q is the mean cross-section of the silver halide grains. The equation is mainly useful for faint lines (38). The Franzen-Maurer-Schuy equation (44) is derived theoretically and is based on the Kinoshita equation (38). It takes the form:

$$\log\ (\text{ion intensity}) = \log\left[\left(\frac{1 - T_s}{T_\ell - T_s}\right)^{1/V} - 1\right] - \log \frac{e}{V(1 - T_s)} \qquad \text{(IV-4)}$$

or

$$T_\ell = T_s + \frac{1 - T_s}{\left(1 + \frac{e(\text{ion intensity})}{V(1 - T_s)}\right)^V} \qquad \text{(IV-5)}$$

where e is a measure of the sensitivity of the emulsion and V is a measure of the slope of the calibration curve. This equation is useful over the entire range of the calibration curve (38,195).

These methods of calibration all have both advantages and disadvantages. The "many isotope method" can be used only if at least one of the useful elements is in the sample with a sufficiently high concentration (38). The Churchill method uses only one element to determine the curve (234) and does not take into account the dependence of the emulsion response to ion mass (38,195,217), line width variation with ion mass (217), emulsion and background variations across the photoplate (38,195), instrumental mass discrimination (38), and errors in tabulated isotopic abundance values (38,195). Small errors in the measurement of the ion intensity ratios can be magnified to the tenth to twentieth power (195). However, one advantage of this method is that it does not presuppose the shape of the calibration curve like the methods based on mathematical formulae do (217). The linearization transformations are generally useful for only limited sections of the curve (38). The Hull equation has a number of advantages. It uses much more data to construct the calibration curve than used by the graphical methods (195), the magnitude of the working range of the curve is 1000 (231), the equation is useful in computer applications (38,195,235), but the equation is useful for only singly charged ions (38). The Kinoshita formula includes a number of theoretical factors, but is useful for only faint lines (38). The Franzen-Maurer-Schuy formula also has a number of advantages like the Hull and Kinoshita formulae (38,235). This formula uses a large quantity of data to construct the calibration curve, includes a number of theoretical factors, is useful in computer applications and for singly and multiply charged ions, and the working range extends over the entire curve.

The method of emulsion calibration chosen for the research project described in this dissertation was a computer application of the Franzen-Maurer-Schuy formula. The steps in the calibration procedure were:

1. Set the value of T_s to 0.005.
2. Calculate V from the transmittance values for each isotopic pair using the Franzen-Maurer-Schuy formula.
3. Average the values of V for the pair.
4. Calculate the isotopic abundance ratio using the Franzen-Maurer-Schuy formula for each pair using the average value of V.
5. Compare the calculated ratio to the actual ratio for each pair and calculate deviations.
6. Average the deviations.
7. Increase and decrease T_s by steps and repeat the procedure for each step until a minimum average deviation is found.

The value of T_s and average V which produce the minimum average deviation are the saturation and slope parameters for the photoplate. Thirty-one photoplates from the same batch containing the mass spectra for the ash and ashed coal samples analyzed for this research project were calibrated. The isotopic pairs selected for the calibration were

$^{63,65}Cu^{+2}$, $^{135,137}Ba^{+2}$, $^{90,91}Zr^{+1}$, $^{135,138}Ba^{+1}$, $^{136,138}Ba^{+1}$, and $^{137,138}Ba^{+1}$. These pairs were selected because of their freedom from spectral interferences and each ratio of their abundances was greater than 1.5 but less than 20. The transmittance values of the spectral lines used were at least 20% darker than background (i.e., T_b = 80%, faintest T_ℓ measured was 60%). Also, a few transmittance values close to saturation were used to better approximate T_s. Emulsion variation between plates of the same batch has been shown to be slight when compared to other sources of error in the calibration procedure (176, 185,218,219,236). The data from the 31 photoplates were combined for each isotopic pair. The data for the three Ba^{+1} pairs were combined because of the close proximity of the spectral lines. The data for each set of pairs were averaged and "bad data" were excluded using the Chauvenet criterion for rejection (237). The calibration results are reported in Table IV-2. The increase in V and the slight increase in T_s with increasing m/z ratio are surprising. The increase in V

Table IV-2. Photoplate calibration results

	Cu^{+2}	Ba^{+2}	Zr^{+1}	Ba^{+1}
Av. V	1.073	1.385	1.652	2.275
% rel. std. dev.	8.0	2.5	7.1	22.1
Av. T_s	0.0067	0.0077	0.0080	0.0084
Range	0.004- 0.009	0.006- 0.010	0.005- 0.011	0.006- 0.011

indicates an increase in the slope of the calibration curve with increasing m/z ratio (38). The slight increase in T_s indicates that the dependence of T_s on the m/z ratio is minor. These results contradict the results reported by other researchers (46,47,176,222, 224,227,230,235,238,239). These researchers found an overall decrease in slope and a significant increase in T_s for increasing m/z ratios. Their results indicate an overall decrease in the sensitivity of the emulsion with increasing m/z ratio while the results reported here indicate an overall increase in sensitivity.

To verify the results, the calibration curves for the four sets of isotopic pairs were constructed using the Churchill method (216). The curves are shown in Fig. IV-2. The curves do verify the overall increase in slope and the relative insignificance of the slight increase in T_s. The average value of V increases linearly with $(m/z)^{1.5}$ as defined by:

$$V = (8.60 \times 10^{-4})(m/z)^{1.5} + 0.905 \qquad \text{(IV-6)}$$

A theoretical explanation of the observed increase in sensitivity with increasing m/z ratio is provided by interactions between energetic ions and matter observed in nuclear and radiochemistry (240). The penetration of an ion into a substance is directly proportional to its momentum, but inversely proportional to the square of the charge on the ion. The greater the penetration of the ion into the photographic emulsion, the more sensitive the emulsion is to the detection of that ion and the greater the value of V. For SSMS work, these quantities can be stated mathematically by:

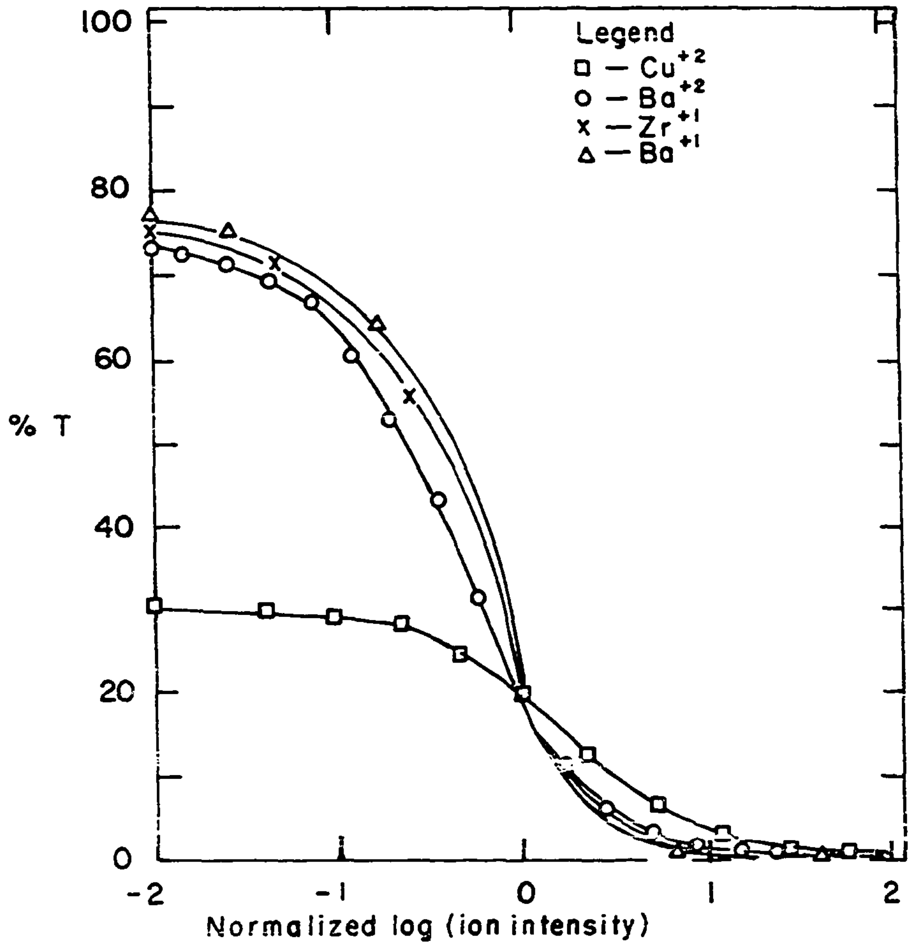

Figure IV-2. Photoplate calibration curves (Churchill method)

mv = momentum of ion

z^2 = coulombic force

Pz = kinetic energy of ion, where P is the acceleration potential

$$\frac{mv}{z^2} \cdot Pz = \frac{mvP}{z} \qquad \text{(IV-7)}$$

The value of P is constant for all of the ions formed in the ion source, thus:

$$V \alpha \frac{mv}{z} \qquad \text{(IV-8)}$$

The average values of V are plotted versus $(m/z)^{1.5}$ and $(mv/z)^{1.0}$ in Fig. IV-3. These plots illustrate that this theoretical explanation for the observed increase in V with increasing m/z ratio is valid. Equation IV-6 was used to determine the value of V to be used in the calculation of the intensity of each ion using the Franzen-Maurer-Schuy formula. The quantity T_s was set equal to 0.008 for all of the ions because of the insignificance of its variation across the photoplate. This insignificance is shown by the ranges of T_s for each set of isotopic pairs in Table IV-2. The ranges of T_s values covered by all of the sets of pairs are nearly the same.

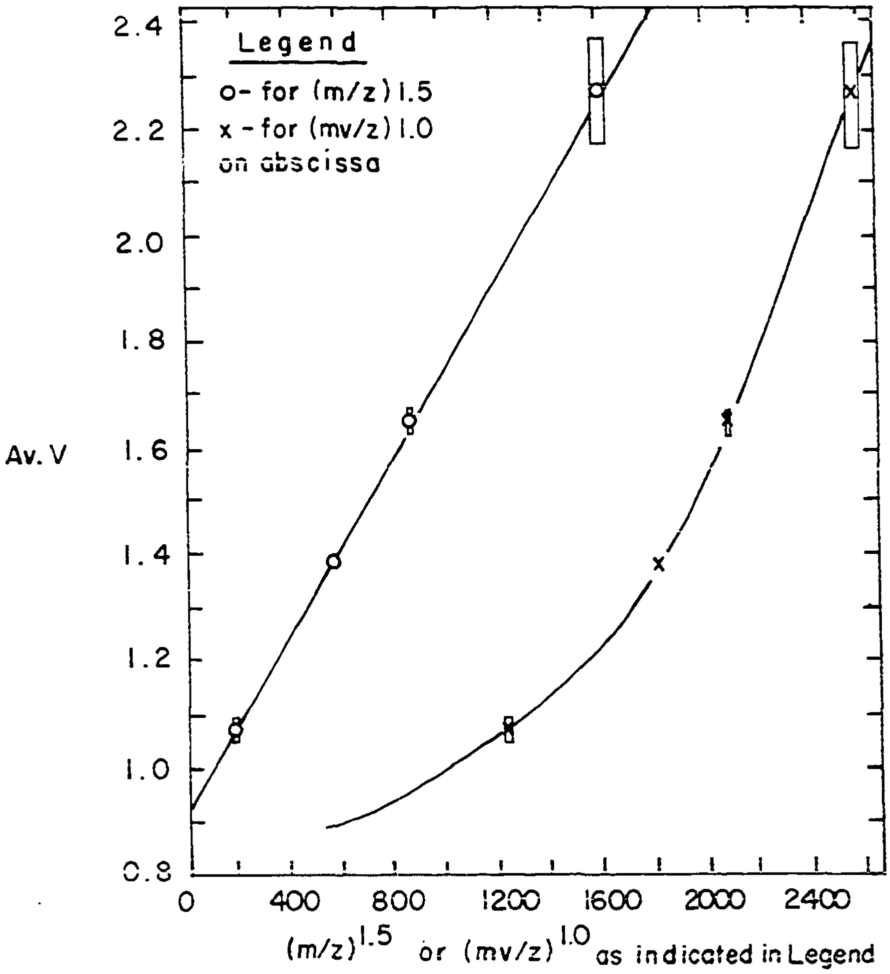

Figure IV-3. Dependence of V on ion mass and energy

V. ANALYSIS OF STANDARD AND IOWA STATE UNIVERSITY POWER PLANT COAL AND ASH SAMPLES BY SSMS

A. Experimental

1. Instrumentation

The analyses of the coal and ash samples collected for this project were performed using a GRAF 2.2 spark source mass spectrograph manufactured by Nuclide Corp., State College, PA. The instrument was modified here for automatic control of the spark and illumination angle of the ion optical axis. The photographic plates used to record the mass spectra were Ilford Q-2 plates manufactured by Ilford Ltd., Manchester, U.K. The mass spectral lines were read with a microphotometer manufactured by Jarrell-Ash Co., Newtonville, MA, Model #2100. The analytical data were processed by a LSI-11 microprocessor computer system.

2. Sampling procedure

The Iowa State University Power Plant burns a mixture of high-sulfur Iowa coal and low-sulfur Colorado coal to meet the sulfur emission standards of the Environmental Protection Agency (EPA) with minimal fuel costs. The Iowa and Colorado coals are shipped from mines located near Lovilia, Iowa, and Craig, Colorado, respectively. The plant has six boilers and arrangements were made for the collection of coal and ash samples from boiler #4. Boiler #4 is a spreader-stoker unit in which approximately 40% of the ash left after combustion is carried out of the combustion zone with the flue gas (241). The remaining 60%, the heavy ash fraction, falls below the boiler grates as bottom ash. The fly ash first encounters a primary dust collector (PDC), which is approximately 85% efficient, and then an electrostatic precipitator (EP), which is approximately 97% efficient. The relative distribution of the total ash collected is approximately 60% bottom ash, 34% primary dust collector fly ash, and 6% electrostatic precipitator fly ash. The plant burned only the Iowa coal in this boiler during August, 1979, and only the Colorado coal during September, 1979. The schedule for the collection of the coal and ash samples is reported in Table V-1. Twelve samples were collected for each type of sample.

Procedures used for the collection of the Power Plant samples and their preparation for analysis were according to American Society for Testing and Materials (ASTM) standard test methods (242,243). The sampling method used for the raw coal was adapted from test method D2234-76. The top size of the coal entering the boiler was less than 50 mm, so 35 increments, weighing 3 kg each, were collected per sample. The increments were combined and the size of the gross sample was reduced using a procedure adapted from test method D2013-72. The gross sample was coned and quartered down to a weight of 12 kg. The sample was crushed using a jaw crusher to a size which would pass through a No. 4 sieve. The size of the sample was reduced using a riffle to a weight of 4 kg and then the sample was ground using a face grinder to a size which would pass through a No. 20 sieve. The size was then reduced to a weight of 500 g and the sample was ground again to a size which would pass

Table V-1. Schedule for power plant sampling

Sample type	Date sampled	No. of samples collected
Iowa Coal	8/15/79	4
	8/16/79	4
	8/17/79	4
Bottom Ash	8/15/79	4
	8/16/79	4
	8/17/79	4
Fly Ash-PDC	8/15/79	4
	8/16/79	4
	8/17/79	4
Fly Ash-EP	8/15/79	4
	8/16/79	4
	8/17/79	4
Colorado Coal	9/19/79	4
	9/20/79	4
	9/21/79	4
Bottom Ash	9/19/79	4
	9/20/79	4
	9/21/79	4
Fly Ash-PDC	9/19/79	4
	9/20/79	4
	9/21/79	4
Fly Ash-EP	9/19/79	4
	9/20/79	4
	9/21/79	4

through a No. 60 sieve. The sample was riffled to a final weight of 50 g. All of the ash samples were collected using a procecure adapted from test method C311-77. The ash samples were collected from their respective hoppers in one-liter polyethylene bottles. The gross sample weight was at least 2 kg. The size and weight of the samples were reduced using the same procedure used for the coal samples.

Eleven standard coal samples were acquired from sources and locations reported in Table V-2. These samples were selected because they come from different and diverse geographical areas and their trace elemental concentrations cover a broad range of values. One standard ash sample (SRM 1633) was acquired from the National Bureau of Standards (NBS). Large amounts of organic material in samples analyzed by SSMS can adversely affect the analytical results (201,244,245). The ashing method selected for the coals was low-temperature ashing (LTA) (246-249). The samples are placed in Pyrex boats which are placed inside the ashing chambers. A high frequency electromagnetic field, produced by a radio frequency oscillator, surrounds the samples. The chambers are evacuated and dry oxygen gas enters the chambers. The oscillator is turned on and the field produces a reactive oxygen species which oxidizes the organic material. The chambers are pumped to remove the reaction products and maintain a fresh supply of oxygen. The temperature of the sample usually does not exceed 200°C because the oxidizing process is a slow chemical reaction (246,247). A dry ashing method was chosen because reagents used in wet ashing methods can add contaminants to the samples (250,251). This low-temperature method was chosen because the majority

Table V-2. Standard coal samples

Source	Sample No.	Origin	Location
National Bureau of Standards	SRM 1632-coal	---	---
	SRM 1635-subbituminous coal	---	---
Illinois State Geological Survey	C13464	Herrin #6	Williamson County, IL
	C16030	Herrin #6	
	C16408	Chapel #8	
United States Geological Survey	PAS16	Upper Freeport Bed	Westmoreland County, PA
	PAS47	Pittsburgh Bed	Washington County, PA
	D160984	Wyodak Anderson Bed	Campbell County, WY
	D165578	Beulah Bed	Mercer County, ND
	D165762	Pust Bed	Richland County, MT
	D165766	Pust Bed	Richland County, MT

of elements of interest are not lost by diffusion or volatilization and the sample is less likely to be contaminated by the atmosphere or sample container than when high-temperature methods are used (61,251). This ashing method is useful for analyses performed by SSMS (251). A disadvantage of this method is the need for periodic stirring of the samples to ash them completely (248). The oxidation reaction occurs only on the surface of the sample and the time needed to complete the ashing is relatively long. All of the standard coal and Power Plant coal and ash samples were ashed to remove the majority of the organic material. All of the ashed samples were crushed using a boron carbide mortar and pestle to a size which would pass through a No. 170 sieve and thoroughly mixed using a vibrating mixer/mill. The samples were stored in 30 mL polyethylene bottles.

3. Analysis procedure

The samples were selected at random for analysis. Equal weights of the sample and spectroscopically pure graphite, manufactured by National Carbon Co., New York, NY, Grade SP-1, were mixed using a vibrating mixer/mill. Electrodes were formed from the sample-graphite mixture and sparked using the same procedures described in Chapter IV of this dissertation.

B. Results and Discussion of the Analysis of the Standard Samples

As stated in Chapter I, the sensitivity of the SSMS method of analysis is not the same for all of the elements. This difference in sensitivity can be corrected for by applying a sensitivity coefficient to the analytical results. The elemental values of the coefficients are calculated relative to that of an internal standard which is given a coefficient of 1.0. The elemental relative sensitivity coefficients (RSC) are calculated using:

$$\mathrm{RSC}_x = \frac{(\mathrm{ppma}_x)(\mathrm{ATWT}_x)(\mathrm{ppmw}_{\mathrm{std}})}{(\mathrm{ppma}_{\mathrm{std}})(\mathrm{ATWT}_{\mathrm{std}})(\mathrm{ppmw}_x)} \qquad \text{(V-1)}$$

where ppma_x and $\mathrm{ppma}_{\mathrm{std}}$ are the concentrations of element X and the internal standard, respectively, determined by SSMS in units of ppm atomic, ATWT_x and $\mathrm{ATWT}_{\mathrm{std}}$ are the atomic weights of element X and the internal standard, and ppmw_x and $\mathrm{ppmw}_{\mathrm{std}}$ are the concentrations expressed in units of ppm by weight. To determine the RSC values for the elements of interest in a particular sample matrix, well-characterized standard samples with a similar matrix must be available. The RSC values for 62 elements in ashed coal and ash were calculated using the analytical results from the SSMS analysis of the standard coal and fly ash samples described earlier in this chapter and the ppm by weight values reported by the sources of the standards. Some requirements which the selected internal standard should satisfy are (187):

1. The element should be homogeneously distributed throughout the sample.
2. An independent method which is capable of accurate analysis of the element should be available.
3. The elemental concentration should be representative of the trace elemental concentrations in the sample.
4. The elemental concentration should be such that mass spectral lines with transmittance values on the linear portion of the calibration curve are available.
5. The elemental lines should have no spectral interferences.
6. The mass spectral lines should appear in regions of the photoplate with minimal background fog.
7. The element should be multiisotopic and have multiply charged lines available for obtaining accurate analytical results.
8. The element should be representative of the different groups of the periodic table.
9. The element should have a vapor pressure representative of the elements in the sample.
10. The element should be representative of the different chemical species in the sample.
11. In the case of coal and ash samples, the element should be representative of the elemental organic-inorganic affinities.

No one element can satisfy all of these requirements. Three elements were selected for use as internal standards, Cu, Zr, and Ba. All three are multiisotopic with singly and multiply charged spectral lines which are free of interferences and appear in good regions of the photoplate. Barium is the most volatile and has the highest organic affinity (91) of the three. Copper is intermediate in both cases and zirconium is refractory and present in the mineral phase of the coal.

The average elemental RSC values based on Cu as the internal standard, the relative standard uncertainty in the averages, and the number of analyses from which the averages were determined are reported in Table V-3 for the ashed coal and ash matrices. One analysis of each of the eleven coal standard samples and five analyses of the one fly ash standard sample were performed. The average values were calculated, "bad data" were excluded on the basis of the Chauvenet criterion for rejection, and then final average values were computed. No RSC values are reported for S and Cl because of their variable loss during the ashing of the coal samples (61,199,248). The RSC values from the analyses of the fly ash were used for these elements in the subsequent analyses of ashed coal samples. The RSC values from the analyses of the fly ash were also used for Sn, Lu, Hf, Ta, and W in subsequent analyses because none of the sources of the standard coal samples reported concentrations for these elements. The RSC values reported for Pr, Sm, Gd, and Er are based on the values for Nd and Dy, and the values for Ho and Tm are based on the values for Eu and Tb because of the lack of concentrations reported by the sources for these elements. The RSC

Table V-3. Relative sensitivity coefficients (RSC) using Cu as internal reference

	Coal			Fly Ash		
Element	RSC	% Rel. std. uncertainty	No. of analyses	RSC	% Rel. std. uncertainty	No. of analyses
Li	2.2	28	7	11	41	5
Be	11	40	4	40	29	3
B	0.71	10	11	1.6	19	4
F	0.25	23	9	1.8	11	4
Na	1.5	11	9	2.0	16	5
Mg	0.55	5	8	0.84	20	5
Al	0.44	15	11	0.94	13	5
Si	0.57	5	9	0.91	15	5
P	0.89	25	9	0.44	57	5
S	---	---	---	0.88	16	5
Cl	---	---	---	1.9	15	4
K	1.5	7	6	1.8	11	5
Ca	1.5	4.5	10	2.0	16	5
Sc	1.1	5	8	1.1	12	5
Ti	0.52	12	10	0.57	17	5
V	0.73	13	11	1.0	9	5
Cr	1.5	12	10	1.4	5.4	4
Mn	1.8	13	10	2.0	10	5
Fe	0.59	12	10	0.78	9	5
Co	0.68	5.4	9	1.0	10	5
Ni	1.6	19	8	0.75	6.6	4
Cu	1.0	---	---	1.0	---	---
Zn	1.7	7	9	4.2	16	5
Ga	1.9	8.4	8	1.5	15	5
Ge	2.8	36	5	2.2	11	4
As	1.9	11	10	1.7	12	5
Se	1.4	20	11	2.8	10	5
Br	0.022	2.5	5	1.3	10	5
Rb	1.4	22	4	2.1	11	4
Sr	0.22	5.4	6	0.83	20	5
Y	0.73	6.4	7	0.81	10	5
Zr	0.28	13	9	0.62	8	5
Mo	0.66	21	9	1.3	26	5
Cd	1.9	8.5	5	2.7	8	5
Sn	---	---	---	1.2	18	5
Sb	1.4	15	11	1.7	8	4
I	0.77	25	3	2.2	10	4
Cs	2.0	15	3	3.5	22	5
Ba	0.35	11	10	0.70	15	5
La	0.17	8	8	0.54	13	5

Table V-3. (Continued)

Element	Coal			Fly Ash		
	RSC	% Rel. std. uncertainty	No. of analyses	RSC	% Rel. std. uncertainty	No. of analyses
Ce	0.13	10	5	0.61	16	5
Pr	0.43	24	---	1.3	19	---
Nd	0.34	34	2	1.0	21	5
Sm	0.45	24	---	1.3	22	5
Eu	1.4	23	5	2.7	20	5
Gd	0.45	24	---	1.5	19	5
Tb	1.4	14	4	1.9	31	4
Dy	0.53	31	3	1.6	20	5
Ho	1.4	8	---	3.6	20	5
Er	0.45	24	---	1.4	19	---
Tm	1.4	13	---	1.6	24	5
Yb	1.4	21	4	1.2	31	5
Lu	---	---	---	1.2	27	4
Hf	---	---	---	0.95	30	5
Ta	---	---	---	0.50	28	4
W	---	---	---	1.2	27	5
Hg	1.3	19	3	6.5	22	---
Tl	3.0	18	3	4.3	15	5
Pb	0.71	10	6	2.1	14	5
Bi	1.0	7	---	1.8	24	4
Th	0.80	17	6	1.9	14	4
U	1.4	11	8	2.2	11	4

values for these rare earths should be similar to those for Nd and Dy, and Eu and Tb (180). The RSC value for Bi in the coals is based on the values for Pb, Th, and U because of its physical similarity to these other high-mass elements and again no concentrations for this element were reported by the sources. The RSC values for Pr and Er in the fly ash are based on the values for Nd, Gd, and Dy for the same reasons as stated previously for the coals. The RSC value for Hg is based on experimental observations of in-house analytical measurements and the compilation of observations by other laboratories (187). The standard uncertainties for Li and Be are relatively high because they are monoisotopic and have only one mass spectral line located in a region of the photoplate with high background fog and subject to spectral aberrations. The uncertainties for B, F, Na, and Mg are relatively high because of the high background fog. The uncertainty for P is high in the coals because of its variable loss during ashing (250) and in the fly ash because its concentration is not well known (253). Inhomogeneity may be the reason for the relatively high uncertainties for Ni and Rb in the coals, Sr in the fly ash, and Mo in both. Variable losses during ashing may be a reason for the high uncertainties for Ge and Se in the coals because of their association with the organic fraction (91). Inhomogeneity may also be a problem. The uncertainty for Sn may be high in the ash because of its low concentration. The uncertainty for I is high in the coals because of its variable loss during ashing (61,199, 246,251,254). The uncertainty for Cs is relatively high in both the coals and fly ash because its volatility and low first ionization potential makes its behavior during sparking erratic. The uncertainties for the rare earths in the coals and ash are high possibly because of inhomogeneity and their low concentrations. The uncertainty for Hg is high because of its loss during ashing (61,199,246,249,251,254) and erratic behavior in the spark due to its volatility. The uncertainties for Tl and Bi may be high because of their low concentrations and the volatility of Tl.

The plots of the precision of the elemental RSC data *versus* the logarithm (log) of the elemental concentration are shown in Figs. V-1 and V-2 for the coal and fly ash standard samples. As expected, the precision is worst at low and high concentrations with the best precision obtained for concentrations near 100 ppm. The precision is better than ±30% for elemental concentrations ranging from 5 to 2500 ppm in the standard coal samples and better than ±20% for concentrations ranging from 10 ppm to 1% in the standard fly ash sample. The precisions are generally better for the fly ash than the coals, probably because of the better homogeneity of the sample.

C. Results and Discussion of the Analysis of the Power Plant Samples

The concentrations for 62 elements in the Iowa and Colorado coal, bottom ash, fly ash-PDC, and fly ash-EP were calculated using a rearrangement of Equation V-1:

$$\mathrm{PPMW}_x = \frac{(\mathrm{ppma}_x)(\mathrm{ATWT}_x)(\mathrm{ppmw}_{std})}{(\mathrm{ppma}_{std})(\mathrm{ATWT}_{std})(\mathrm{RSC}_x)} \qquad (V\text{-}2)$$

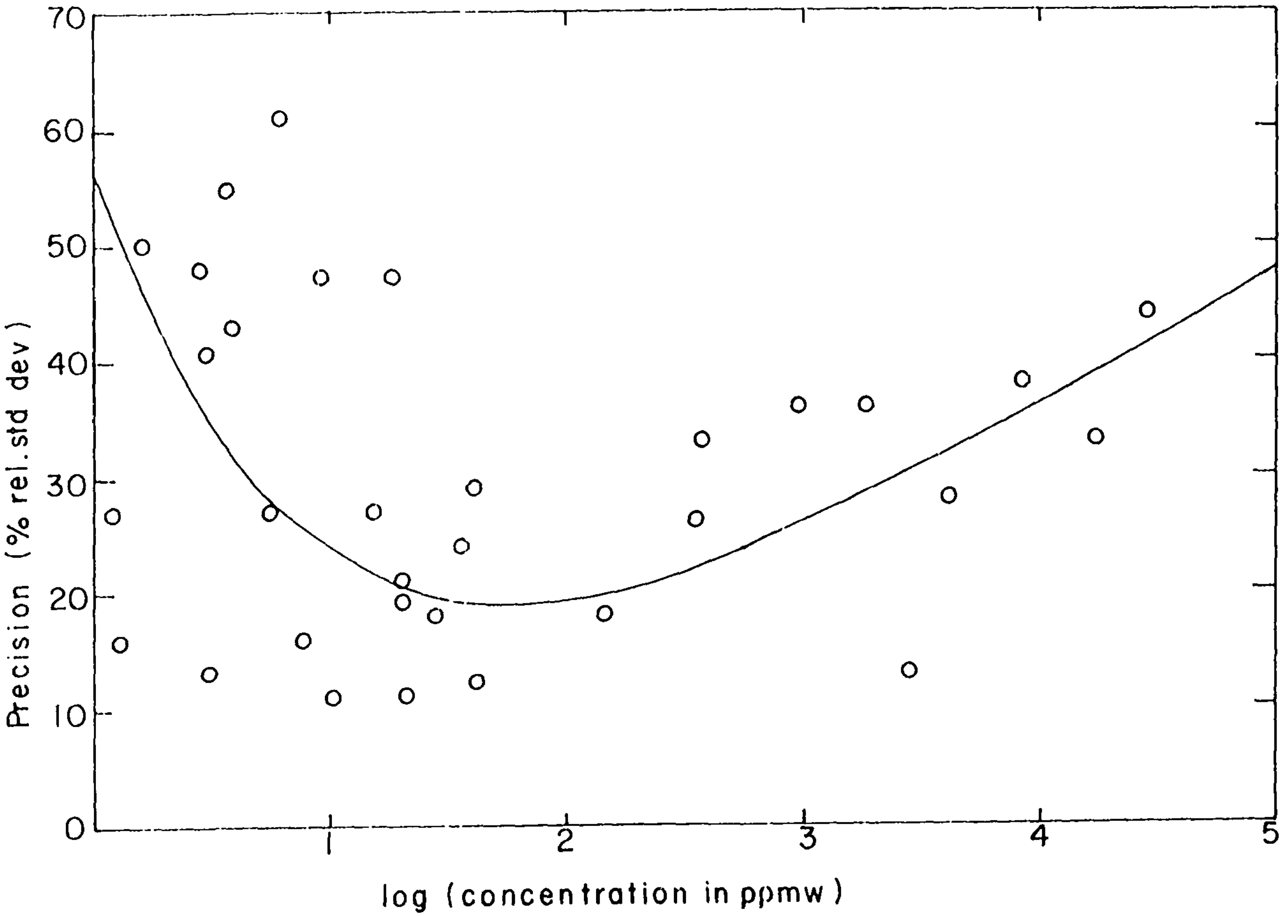

Figure V-1. Precision of RSC values *vs*. log (concentration) for coal standard samples

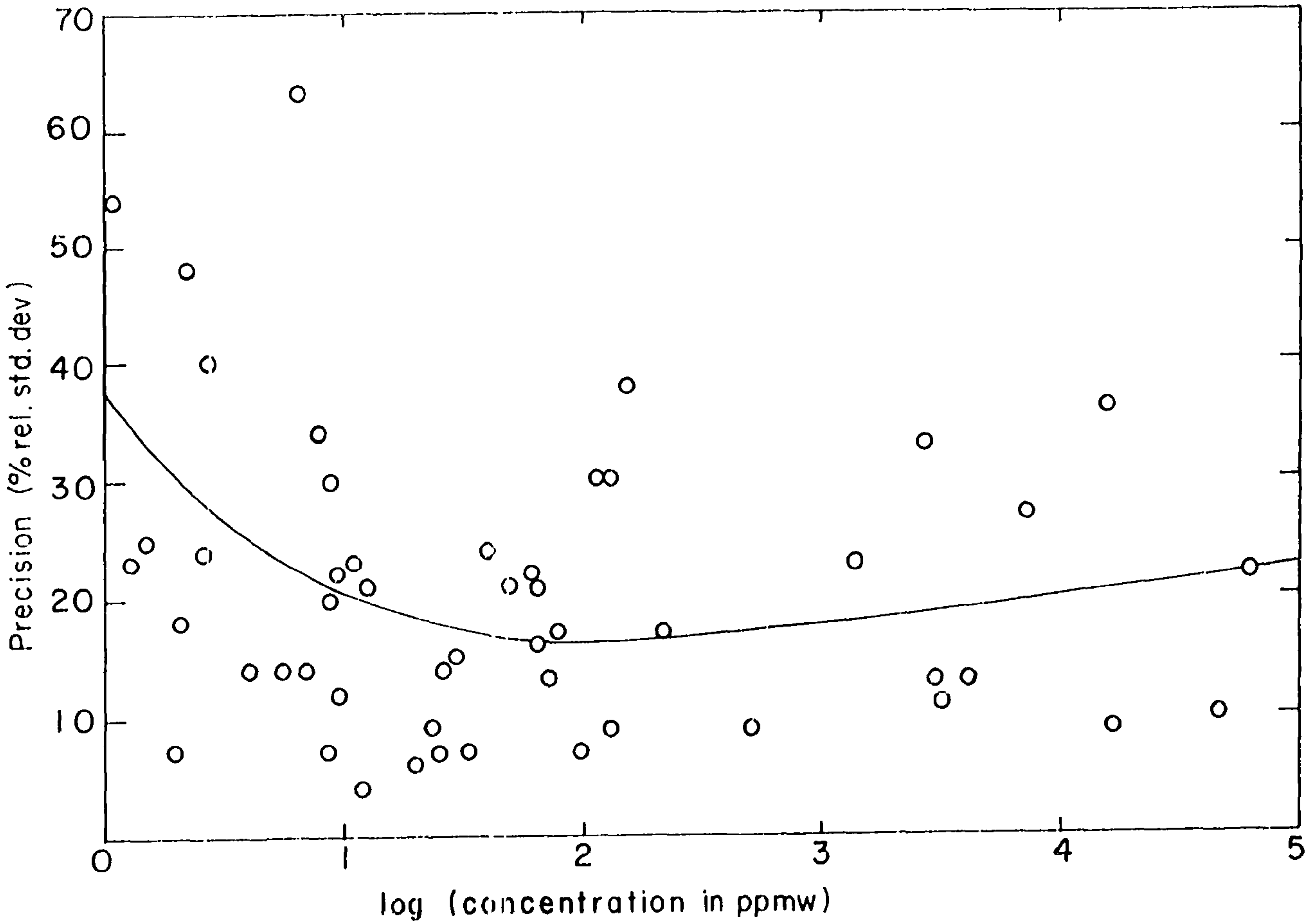

Figure V-2. Precision of RSC values vs. log (concentration) for fly ash standard sample

The RSC values based on the coal standard samples and ash standard sample were used to calculate the elemental concentrations in the coal and ash samples, respectively. The concentrations of the three internal standards were determined independently by wet chemical methods. Copper and barium were determined by flame atomic absorption and zirconium was determined spectrophotometrically. One of the twelve samples from each of the eight types of sample was analyzed for Cu, Zr, and Ba. The results of these analyses are reported in Table V-4. Samples from the Iowa and Colorado coals are abbreviated IA and CO, respectively.

Elemental concentrations were calculated based on each of the three internal standards. The calculations resulted in 12 concentrations for an element in the Iowa coal, bottom ash, fly ash-PDC, fly ash-EP, Colorado coal, bottom ash, fly ash-PDC, and fly ash-EP based on the Cu, Zr, and Ba internal standards for each of the 62 elements. The concentrations for each population of 12 were averaged and "bad data" were excluded on the basis of the Chauvenet criterion for rejection. The average concentration for an element based on one of the internal standards was compared to the averages based on the other two internal standards using the t-test for the consistency of two means at the 95% confidence level (237). Details of the computer program which performed these calculations and a complete listing of the results are not given here because of the large volume of the program and data listings. The reader may contact Professor Harry J. Svec, 21 Gilman, Iowa State University, Ames, Iowa 50011, for details.

Table V-4. Results of wet chemical analysis

Sample	Cu (ppmw)	Zr (ppmw)	Ba (ppmw)
IA coal	35	132	248
CO coal	38	134	346
IA bottom ash	65	229	225
CO bottom ash	133	181	517
IA fly ash-PDC	50	212	265
CO fly ash-PDC	79	237	181
IA fly ash-EP	224	322	462
CO fly ash-EP	296	485	538

The elemental precisions for the Power Plant samples were combined with those for the coal and ash standard samples to make a comparison between the values based on the three internal standards. The results are reported in Table V-5. Approximately 50% of the elemental precisions based on Cu and Zr are better than ±30%, but less than 25% of the values based on Ba are better than ±30%. A possible explanation is that the Ba in the samples is not homogeneously distributed. This poor homogeneity diminishes the usefulness of Ba as an internal standard for these analyses. Also, upon further study, it was discovered that the dissolution of these types of samples for the wet chemical analysis of Ba can be problematic (137). More than 10% of the Ba remains in the residue left after dissolution. The homogeneity of the Cu appears to be slightly better than that of the Zr. The results of the t-test comparisons indicated that in many cases the elemental concentrations based on Zr were not of the same population as those based on Cu. A possible explanation is that the amount of Zr in the samples submitted for wet chemical analysis was close to the detection limit (10 μg/50 mL) of the spectrophotometric method (252). The amount of Cu in the samples was sufficiently above the detection limit of the flame atomic absorption method so the accuracy of its analysis which is better than 5% (252) was not questioned. The results of the SSMS analysis for Zr based on Cu as the internal standard and the wet chemical analysis are reported in Table V-6. The wet chemical results are higher than the SSMS results in every case indicating that Zr is not as suitable as Cu for use as an internal standard in these

Table V-5. Comparison of precisions of SSMS analysis between Cu, Zr, and Ba internal references

	Cu		Zr		Ba	
Range of precision (%)	No. of elemental precision values	% of total	No. of elemental precision values	% of total	No. of elemental precision values	% of total
≤ 10	67	11	32	5	6	1
≤ 15	128	22	104	18	31	5
≤ 20	194	33	162	27	59	10
≤ 25	252	43	220	37	93	16
≤ 30	311	53	280	47	136	23

Table V-6. Comparison of wet chemical and SSMS results, using Cu as internal reference, for concentration of Zr

Sample	Wet chemical (ppmw)	SSMS (ppmw)	% Rel. dif.
IA coal	132	121	9
CO coal	132	131	2
IA bottom ash	229	217	6
CO bottom ash	181	157	15
IA fly ash-PDC	212	211	0.5
CO fly ash-PDC	237	226	5
IA fly ash-EP	322	283	17
CO fly ash-EP	485	378	28

particular analyses. The failure of Ba and Zr to be suitable as internal standards precludes any correlations between the three selected internal standards and elements with similar properties and organic-inorganic affinities.

The average elemental concentrations and relative standard uncertainty in the averages are reported in Table V-7 for the Iowa coal samples and Table V-8 for the Colorado samples. The values for 53 of the elements are based solely on Cu as the internal standard, the values for the other 9 are averages of the results based on both Cu and Zr. These nine elements and the relative precision of their RSC values based on Cu and Zr are listed in Table V-9. The precision of the RSC values based on Zr is much better than that for the values based on Cu so the concentrations based on Zr are combined with those based on Cu and the average values are used. The standard uncertainties for Li, Be, B, F, P, and S are relatively high for the same reasons stated previously in the discussion of the RSC values. All of the Power Plant samples were ashed so the standard uncertainties for the halogens are high because of their variable loss during ashing (61,199,251,254), and particularly for the bottom ash because of their low concentrations in that type of sample. The uncertainties for Ni and Ge in the coals are high for the same reasons stated previously in the discussion of the RSC values. The uncertainties for Zn are high because it is not distributed homogeneously in these types of samples (199), and only one mass spectral line is free of interferences. The high uncertainty for As in the Colorado fly ash-PDC is caused by three concentrations being

Table V-7. Results of SSMS analysis of Iowa Power Plant samples[a]

	Iowa Coal							
Element	Whole coal	% Rel. std. uncertainty	Bottom ash	% Rel. std. uncertainty	Fly ash PDC	% Rel. std. uncertainty	Fly ash EP	% Rel. std. uncertainty
Li	1.42	25	6.19	21	5.91	23	7.54	25
Be	0.52	30	3.22	30	1.76	37	2.27	38
B	26.1	15	399	21	292	12	375	11
F	30.4	13	20.5	21	21.9	16	43.0	17
Na	130	8	2180	8	953	8	2710	21
Mg	339	6	4880	10	2690	7	7460	6
Al	0.370%	7	3.40%	10	2.19%	6	4.28%	6
Si	1.36%	4	12.9%	5	13.3%	5	7.41%	6
P	145	10	3690	18	2910	18	4390	19
S	0.958%	20	3.34%	17	0.862%	13	3.96%	21
Cl	4.19	9	14.7	8	22.2	14	35.4	20
K	567	10	7340	7	7710	7	8570	6
Ca	0.718%	3	7.03%	5	3.67%	5	2.36%	5
Sc	1.53	7	14.0	11	11.0	7	22.7	6
Ti	258	5	2460	7	2560	6	4020	6
V	7.61	6	56.2	9	51.0	7	147	6
Cr	5.85	12	56.6	10	48.3	9	64.1	6
Mn	58.0	5	824	5	419	7	118	4
Fe	1.01%	6	11.2%	4	4.76%	4	4.82%	4
Co	3.08	7	16.2	5	17.0	5	47.9	4
Ni	15.4	13	198	9	122	8	376	5
Cu	6.06	---	49.1	---	32.7	---	174	---
Zn	158	27	485	20	611	14	7560	6
Ga	1.50	9	13.7	11	13.8	8	204	5
Ge	6.04	12	32.8	6	47.0	4	481	4

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[a] All concentrations in units of ppm by weight unless indicated otherwise.

Table V-7. (Continued)

	Iowa Coal							
Element	Whole coal	% Rel. std. uncertainty	Bottom ash	% Rel. std. uncertainty	Fly ash PDC	% Rel. std. uncertainty	Fly ash EP	% Rel. std. uncertainty
As	6.57	7	22.1	8	61.0	5	508	6
Se	2.15	9	7.07	7	2.60	7	14.1	4
Br	19.9	9	2.77	20	2.15	7	2.32	14
Rb	4.03	15	43.1	10	35.2	13	60.1	11
Sr	42.9	10	197	14	119	10	317	8
Y	7.54	4	62.3	7	44.8	8	113	7
Zr	20.9	5	164	4	138	4	220	6
Mo	1.65	9	5.03	13	4.98	9	21.2	9
Cd	0.63	18	3.10	20	5.01	4	112	4
Sn	0.36	14	5.73	12	3.29	8	25.1	13
Sb	0.49	9	1.50	6	2.49	5	44.8	4
I	1.12	11	0.87	16	1.72	10	3.88	7
Cs	0.34	14	1.81	15	1.81	19	6.84	14
Ba	37.0	10	341	15	191	6	508	15
La	5.67	12	29.3	13	23.8	9	49.4	6
Ce	15.1	11	53.7	12	44.9	9	113	10
Pr	1.17	13	4.54	11	3.74	10	8.34	10
Nd	7.87	13	29.2	9	28.5	7	65.5	7
Sm	2.21	11	7.64	17	7.64	14	16.4	8
Eu	0.31	8	2.52	14	2.02	11	2.44	10
Gd	2.13	12	8.62	18	7.84	9	14.1	9
Tb	0.18	15	1.88	13	1.93	12	1.64	11
Dy	1.48	15	5.59	21	4.85	11	11.1	9
Ho	0.15	11	0.79	14	0.73	10	0.75	10
Er	0.66	12	1.97	13	1.99	11	3.98	13
Tm	0.06	11	0.58	28	0.51	19	0.81	11
Yb	0.15	17	1.64	12	2.00	19	4.11	13

Table V-7. (Continued)

	Iowa Coal							
Element	Whole coal	% Rel. std. uncertainty	Bottom ash	% Rel. std. uncertainty	Fly ash PDC	% Rel. std. uncertainty	Fly ash EP	% Rel. std. uncertainty
Lu	0.05	15	0.78	21	0.68	16	0.94	12
Hf	0.22	33	1.43	17	2.22	20	3.76	31
Ta	0.14	87	1.50	---	0.71	18	2.62	26
W	0.24	22	1.71	36	1.26	16	2.98	16
Hg	0.28	22	0.71	19	0.30	56	0.70	18
Tl	0.31	13	0.65	33	1.16	7	1.67	6
Pb	19.0	6	35.2	6	84.2	5	1360	5
Bi	---	---	---	---	---	---	2.14	18
Th	0.67	13	5.09	10	3.24	5	4.42	9
U	0.21	14	2.05	14	1.97	6	4.63	6

Table V-8. Results of SSMS analysis of Colorado Power Plant samples[a]

Element	Colorado Coal Whole coal	% Rel. std. uncertainty	Bottom ash	% Rel. std. uncertainty	Fly ash PDC	% Rel. std. uncertainty	Fly ash EP	% Rel. std. uncertainty
Li	5.99	27	17.8	23	9.84	28	15.6	18
Be	1.16	45	6.42	21	1.79	29	1.99	43
B	52.9	18	230	15	338	25	518	10
F	53.4	16	11.1	13	23.6	19	50.4	10
Na	632	10	3040	14	2780	7	11,400	8
Mg	1120	10	8640	8	5270	7	7650	6
Al	0.990%	9	4.96%	12	3.63%	6	3.62%	5
Si	2.96%	4	16.8%	6	14.3%	5	11.0%	6
P	306	33	9100	19	4810	19	8650	17
S	1.90%	18	8.54%	16	1.05%	16	6.29%	19
Cl	6.82	14	19.8	13	21.0	10	54.3	20
K	719	12	9980	13	5440	7	8020	11
Ca	0.284%	4	3.81%	7	1.99%	5	2.52%	6
Sc	2.14	10	24.3	10	18.6	8	21.8	8
Ti	409	5	5040	8	1990	6	4440	6
V	12.5	9	105	10	91.9	8	136	5
Cr	7.20	15	80.6	11	66.9	4	114	11
Mn	20.4	7	274	9	192	5	129	4
Fe	0.861%	6	14.2%	4	6.82%	4	2.28%	5
Co	4.18	4	55.8	4	29.5	4	73.2	4
Ni	16.0	16	502	6	314	10	626	9
Cu	6.61	---	129	---	50.8	---	235	---
Zn	67.2	15	879	6	797	14	11,200	13
Ga	2.37	9	19.5	8	22.8	6	225	6

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[a] All concentrations in units of ppm by weight unless indicated otherwise.

Table V-8. (Continued)

Colorado Coal

Element	Whole coal	% Rel. std. uncertainty	Bottom ash	% Rel. std. uncertainty	Fly ash PDC	% Rel. std. uncertainty	Fly ash EP	% Rel. std. uncertainty
Ge	5.99	16	25.4	6	50.2	5	727	4
As	4.58	9	11.0	12	65.6	19	584	6
Se	3.15	12	9.69	5	4.26	6	18.7	6
Br	17.9	14	2.24	21	1.08	9	2.44	18
Rb	4.91	7	51.2	14	32.3	10	75.7	9
Sr	115	4	263	18	360	11	572	8
Y	3.41	5	65.4	9	57.7	7	54.9	8
Zr	22.8	6	152	7	145	3	300	5
Mo	1.78	7	12.3	11	8.30	9	39.8	8
Cd	1.46	8	1.55	24	9.07	9	184	4
Sn	0.57	12	1.84	15	2.12	7	48.4	6
Sb	0.56	8	2.13	11	4.99	7	75.8	5
I	2.21	14	0.29	9	1.40	10	3.09	6
Cs	0.62	14	2.65	17	2.37	14	6.07	15
Ba	92.6	17	632	14	862	18	1110	17
La	9.21	13	35.8	14	35.0	9	48.5	7
Ce	17.4	10	81.3	9	83.6	16	131	7
Pr	1.57	12	5.60	10	5.14	15	6.63	11
Nd	8.93	11	33.7	13	27.3	11	53.5	7
Sm	1.83	12	6.97	18	9.32	13	16.2	16
Eu	0.16	12	1.62	9	1.75	10	2.37	7
Gd	1.86	12	6.22	16	7.46	12	12.8	7
Tb	0.12	7	1.44	12	1.66	11	2.33	11
Dy	1.86	14	4.59	16	6.62	15	13.3	8
Ho	0.16	14	0.51	9	0.50	7	1.11	11
Er	0.59	14	1.73	15	2.26	13	4.15	9
Tm	0.09	59	0.54	14	0.51	10	0.78	18

Table V-8. (Continued)

	Colorado Coal							
Element	Whole coal	% Rel. std. uncertainty	Bottom ash	% Rel. std. uncertainty	Fly ash PDC	% Rel. std. uncertainty	Fly ash EP	% Rel. std. uncertainty
Yb	0.24	13	1.84	16	2.44	17	3.37	15
Lu	---	---	0.33	26	0.73	12	0.67	19
Hf	---	---	2.11	21	2.03	14	7.38	19
Ta	---	---	1.46	22	0.57	15	2.85	25
W	0.31	28	1.95	18	0.87	20	3.27	12
Hg	1.33	25	0.58	17	0.37	33	1.03	16
Tl	0.33	12	0.45	17	0.64	6	23.7	7
Pb	25.4	5	29.7	6	40.4	5	2070	9
Bi	0.09	---	---	---	---	---	5.42	12
Th	0.56	13	5.76	12	4.86	6	3.41	8
U	0.63	6	3.06	11	4.43	5	7.35	7

Table V-9. Relative precision of RSC values

Element	Coal		Ash	
	Cu (%)	Zr (%)	Cu (%)	Zr (%)
Al	68	33	38	7
Cr	60	19	12	9
Se	91	38	30	12
Br	40	5	23	7
La	47	11	35	17
Ce	50	11	51	38
Ho	---	---	50	7
Lu	---	---	52	25
Tl	---	---	42	14

larger than the other nine by a factor of two. An explanation for this increase is not apparent. The uncertainties for Cd in the bottom ash and Iowa coal are high because of its low concentration. The inhomogeneity of Ba compared to Cu in these samples caused the relatively high uncertainty in the results for Ba. The uncertainties for Cs, Hg, and the rare earths are high for the same reasons stated previously in the discussion of the RSC values. The high uncertainties for Hf, Ta, and W are caused by their low concentrations. No uncertainty is reported for Ta in the Iowa bottom ash because it was detected in only one of the twelve samples. The high uncertainties for Tl in the bottom ash and Bi in the fly ash-EP are caused by their low concentrations. No uncertainty is reported for Bi in the Colorado coal because it was detected in only one of the twelve samples.

A material balance study was performed for the Iowa samples and, also, for the Colorado samples. The completeness of the elemental recoveries was determined using:

$$X = HTA[(0.6 \cdot LTA_B \cdot B) + (0.34 \cdot LTA_P \cdot P) + (0.06 \cdot LTA_E \cdot E)] \qquad (V\text{-}3)$$

and

$$WC = LTA_C \cdot C \qquad (V\text{-}4)$$

where $LTA_{C,B,P,E}$ are the fractions of residue left after the coal, bottom ash, fly ash-PDC, and fly ash-EP are low-temperature ashed; C, B, P, and E are the elemental concentrations in the coal, bottom ash, fly ash-PDC, and fly ash-EP; HTA is the fraction of residue left after the coal is high-temperature ashed; and the numerical factors are the relative distribution of the total ash between the bottom ash, fly ash-PDC, and fly ash-EP hoppers stated previously in the Experimental section of this chapter. The factors LTA_C and HTA put the elemental concentrations on a whole coal basis for the ashed coal and total ash, respectively. The values of LTA and HTA (255,256) are reported in Table V-10. The recovery of each element is determined by comparing the values of X and WC. The results of the material balance study are reported in Table V-11.

The relative uncertainty in the elemental comparisons can be determined using the uncertainties for the RSC values, concentrations, wet chemical analysis of Cu (±5%), LTA factors (no worse than ±5%), HTA factors (approximately ±10% for the Iowa coal, ±20% for the Colorado coal) (255), and the total ash distribution factors (estimated at ±20% for the bottom ash, ±30% for the fly ash-PDC, and ±40% for the fly ash-EP). The relative uncertainties in the total ash distribution factors were estimated from the comparisons of the factors from other materials balance studies (4,79,197). These uncertainties can be combined using the equations for the propagation of uncertainties in computed measurements (257). The relative uncertainty in the comparison for Fe, which has some of the lowest uncertainties associated with it, is ±21% for the Iowa coal and ±27% for the Colorado coal. The difference between the Iowa and Colorado values is caused by the difference in the uncertainties in the HTA factors. The relative uncertainty in the comparison for Be, which has some of the highest uncertainties associated with it, is ±43% for the Iowa coal and ±71%

Table V-10. Ashing factors for Power Plant samples

Sample	LTA	HTA
IA coal	0.173	0.11
Bottom ash	0.756	
Fly ash-PDC	0.653	
Fly ash-EP	0.779	
CO coal	0.174	0.075
Bottom ash	0.969	
Fly ash-PDC	0.643	
Fly ash-EP	0.794	

Table V-11. Results of material balance study[a]

	Iowa Coal			Colorado Coal			
Element	WC	X	% Rel. dif.	WC	X	% Rel. dif.	CO Dif.-IA Dif.
Li	1.42	0.68	-52	5.99	1.12	-81	-29
Be	0.52	0.29	-43	1.16	0.34	-70	-27
B	26.1	39.7	+52	52.9	21.3	-60	-112
F	30.4	2.46	-92	53.4	1.33	-98	-6
Na	130	210	+61	632	259	-59	-120
Mg	339	471	+39	1120	558	-50	-89
Al	3700	3350	-9.6	9900	3320	-67	-57
Si	1.36%	1.40%	+2.4	2.96%	1.17%	-61	-63
P	145	381	+160	306	571	+87	-73
S	0.958%	0.282%	-71	1.90%	0.439%	-77	-6
Cl	4.19	2.04	-51	6.82	1.67	-76	-25
K	567	829	+46	719	624	-13	-59
Ca	7180	6170	-14	2840	2330	-18	-4
Sc	1.53	1.49	-3.0	2.14	1.67	-22	-19
Ti	258	285	+11	409	297	-27	-38
V	7.61	6.59	-14	12.5	7.67	-39	-25
Cr	5.85	5.97	+2.0	7.20	5.85	-19	-21
Mn	58.0	70.8	+22	20.4	17.8	-13	-35
Fe	1.01%	0.948%	-6.1	0.861%	0.825%	-4.2	+2
Co	3.08	2.02	-34	4.18	3.59	-14	+20
Ni	15.4	20.1	+31	16.0	33.4	+109	+78
Cu	6.06	5.62	-7.2	6.61	8.15	+23	+30
Zn	158	105	-34	67.2	110	+64	+98
Ga	1.50	2.77	+84	2.37	2.47	+4.5	-79
Ge	6.04	7.10	+18	5.99	5.69	-4.9	-23
As	6.57	7.09	+7.9	4.58	4.80	+4.8	-3
Se	2.15	0.66	-69	3.15	0.63	-80	-11
Br	19.9	0.28	-99	17.9	0.14	-99	0
Rb	4.03	4.56	+13	4.91	3.47	-29	-42
Sr	42.9	19.6	-54	115	23.6	-79	-25
Y	7.54	6.53	-13	3.41	4.66	+37	+50
Zr	20.9	17.4	-17	22.8	11.9	-48	-31
Mo	1.65	0.66	-60	1.78	0.94	-47	+13
Cd	0.63	1.13	+81	1.46	1.13	-23	-104
Sn	0.36	0.67	+84	0.57	0.36	-38	-122
Sb	0.49	0.49	+0.4	0.56	0.56	0	0

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[a] All concentrations in units of ppm by weight unless indicated otherwise.

Table V-11. (Continued)

Element	Iowa Coal WC	Iowa Coal X	Iowa Coal % Rel. dif.	Colorado Coal WC	Colorado Coal X	Colorado Coal % Rel. dif.	CO Dif.- IA Dif.
I	1.12	0.15	-52	2.21	0.06	-97	-10
Cs	0.34	0.23	-31	0.62	0.21	-66	-35
Ba	37.2	33.0	-11	92.6	55.4	-40	-29
La	5.67	3.15	-45	9.21	2.72	-70	-25
Ce	15.1	5.97	-60	17.4	6.38	-63	-3
Pr	1.17	0.50	-58	1.57	0.41	-74	-16
Nd	7.87	3.42	-57	8.93	2.45	-73	-16
Sm	2.21	0.90	-60	1.83	0.62	-66	-6
Eu	0.31	0.26	-17	0.16	0.13	-20	-3
Gd	2.13	0.96	-55	1.86	0.53	-72	-17
Tb	0.18	0.21	+13	0.12	0.12	0	-13
Dy	1.48	0.62	-58	1.86	0.44	-77	-19
Ho	0.15	0.09	-43	0.16	0.04	-75	-32
Er	0.66	0.23	-65	0.59	0.15	-74	-9
Tm	0.06	0.06	+7.1	0.09	0.04	-54	-61
Yb	0.15	0.21	+41	0.24	0.16	-33	-74
Lu	0.05	0.08	+82	---	---	---	---
Hf	0.22	0.20	-5.8	---	---	---	---
Ta	0.14	0.14	+5.3	---	---	---	---
W	0.24	0.18	-26	0.31	0.13	-60	-34
Hg	0.28	0.06	-78	1.33	0.04	-97	-19
Tl	0.31	0.10	-68	0.33	0.14	-57	+11
Pb	19.0	14.4	-24	25.4	11.7	-54	-30
Bi	---	---	---	0.09	0.02	-72	---
Th	0.67	0.49	-27	0.56	0.40	-29	-2
U	0.21	0.24	+16	0.63	0.28	-55	-71

for the Colorado coal. The relative uncertainties in the comparison for the rest of the elements range between these values for the two coals. In general, the material balance is satisfactory for both the Iowa and Colorado coals. The analytical problems associated with Li, Be, B, Na, Mg, Cs, Ba, W, and Bi were stated previously in the discussions of the uncertainties in the concentrations and RSC values. The relative differences in WC and X for S, Se, Mo, Hg, Tl, and the halogens are appreciably negative for both coals. These elements are lost from the stack (4,78,79,197,254,258-262). The large positive relative differences for P may be caused by inaccurate RSC values, especially for the ashes because the precision of the reported concentration for P in the standard fly ash sample is poor (253). Similarly, the large negative relative differences for many of the rare earths may be caused by inaccurate RSC values, especially for the coals, because of the lack of values reported by the sources of the standard samples for these elements and the fact that the precision of the values that are reported is generally unknown. The large positive and negative differences for Ni and Sr are possibly due to inhomogeneity in the coals which create errors in the RSC values. The large positive differences for K, Ga, Cd, and Sn in the Iowa coal and Y in the Colorado coal are possibly caused by inhomogeneity in those coals. The inhomogeneity of Zn has been mentioned already and some of the Zn may not be recovered because of deposition on the walls of the furnace (263). The differences between the relative differences for the elements in the Iowa and Colorado coals indicate that the relative differences for the elements in the Colorado coal are shifted negatively relative to the Iowa coal. This shift may be due to an inaccurate value for the Colorado HTA factor. Correcting for this shift can improve the relative differences of some of the elements (e.g., Zr and U) to acceptable values. Inaccurate values for the total ash distribution may also cause errors in the relative differences.

The relative elemental enrichment in the three types of ashes from the two types of coal are reported in Table V-12. The values are calculated using:

$$\text{relative enrichment}_{B,P,E} = \frac{LTA_{B,P,E} \cdot B,P,E}{(LTA_B \cdot B) + (LTA_P \cdot P) + (LTA_E \cdot E)} \qquad (V\text{-}5)$$

where the symbols are the same as in Equation V-3. The elements which form refractory compounds and are associated with the mineral fraction of the coal, such as Be, Ca, Mn, and Fe, are enriched in the bottom ash (79,91,258). Sulfur is enriched in the bottom ash because of the involatile metal sulfates present in the coal and enriched in the fly ash-EP because of the organic sulfur and volatile metal sulfides which vaporize in the furnace and condense on the fly ash as the gases cool (258,268). The enrichments of Na, V, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Mo, Cd, Sn, Sb, Cs, Ba, W, Hg, Tl, Pb, Bi, U, and the halogens in the fly ash-EP may be due to the vaporization of compounds of these elements or the elements themselves in the furnace and their condensation on the surface of the fly ash as the gases cool (4,5,18,79,82, 115,137,197,254,258,264-272). Also, some of these elements, such as V, Ni, Co, Cu, Ga, Ge, Se, Mo, Sb, and U, are associated with the

Table V-12. Relative elemental enrichment

	Iowa Coal			Colorado Coal		
Element	Bottom ash	Fly ash PDC	Fly ash EP	Bottom ash	Fly ash PDC	Fly ash EP
Li	0.315	0.301	0.384	0.412	0.228	0.360
Be	0.445	0.242	0.313	0.630	0.176	0.195
B	0.375	0.274	0.352	0.211	0.311	0.477
F	0.240	0.256	0.504	0.131	0.277	0.592
Na	0.278	0.122	0.601	0.176	0.161	0.662
Mg	0.324	0.179	0.497	0.401	0.244	0.355
Al	0.345	0.222	0.433	0.406	0.297	0.297
Si	0.385	0.395	0.221	0.399	0.340	0.261
P	0.336	0.265	0.400	0.403	0.213	0.385
S	0.413	0.105	0.482	0.538	0.066	0.396
Cl	0.204	0.307	0.490	0.208	0.221	0.571
K	0.311	0.326	0.363	0.426	0.232	0.342
Ca	0.538	0.281	0.181	0.458	0.239	0.303
Sc	0.293	0.231	0.475	0.376	0.287	0.337
Ti	0.273	0.283	0.444	0.440	0.173	0.387
V	0.221	0.200	0.579	0.315	0.277	0.408
Cr	0.335	0.286	0.379	0.308	0.255	0.437
Mn	0.605	0.308	0.087	0.461	0.323	0.216
Fe	0.539	0.229	0.232	0.610	0.292	0.098
Co	0.200	0.209	0.591	0.352	0.186	0.462
Ni	0.284	0.175	0.540	0.348	0.218	0.434
Cu	0.192	0.127	0.681	0.311	0.122	0.567
Zn	0.056	0.071	0.873	0.068	0.062	0.870
Ga	0.059	0.060	0.881	0.073	0.085	0.842
Ge	0.058	0.084	0.858	0.032	0.063	0.906
As	0.037	0.103	0.859	0.017	0.099	0.884
Se	0.297	0.109	0.593	0.297	0.131	0.572
Br	0.382	0.297	0.321	0.389	0.188	0.423
Rb	0.311	0.254	0.434	0.322	0.203	0.476
Sr	0.311	0.189	0.516	0.220	0.301	0.479
Y	0.283	0.204	0.513	0.367	0.324	0.308
Zr	0.314	0.264	0.422	0.255	0.243	0.502
Mo	0.161	0.160	0.679	0.204	0.137	0.659
Cd	0.026	0.042	0.933	0.008	0.047	0.946
Sn	0.168	0.096	0.736	0.035	0.040	0.924
Sb	0.031	0.051	0.918	0.026	0.060	0.914
I	0.134	0.266	0.599	0.060	0.292	0.647
Cs	0.173	0.173	0.654	0.239	0.213	0.548
Ba	0.328	0.184	0.488	0.243	0.331	0.427

Table V-12. (Continued)

	Iowa Coal			Colorado Coal		
Element	Bottom ash	Fly ash PDC	Fly ash EP	Bottom ash	Fly ash PDC	Fly ash EP
La	0.285	0.233	0.482	0.300	0.294	0.407
Ce	0.254	0.212	0.534	0.275	0.282	0.443
Pr	0.273	0.225	0.502	0.322	0.296	0.382
Nd	0.237	0.231	0.532	0.295	0.238	0.467
Sm	0.241	0.242	0.517	0.214	0.287	0.499
Eu	0.361	0.290	0.349	0.282	0.305	0.413
Gd	0.282	0.256	0.461	0.235	0.282	0.483
Tb	0.344	0.355	0.302	0.266	0.306	0.429
Dy	0.260	0.226	0.514	0.187	0.270	0.543
Ho	0.349	0.322	0.329	0.241	0.237	0.522
Er	0.243	0.250	0.502	0.212	0.277	0.511
Tm	0.308	0.269	0.427	0.294	0.277	0.429
Yb	0.212	0.258	0.531	0.241	0.319	0.440
Lu	0.325	0.284	0.391	0.146	0.490	0.365
Hf	0.193	0.300	0.508	0.149	0.215	0.635
Ta	0.311	0.147	0.542	0.253	0.147	0.600
W	0.287	0.212	0.501	0.320	0.144	0.537
Hg	0.414	0.176	0.410	0.292	0.186	0.522
Tl	0.187	0.334	0.479	0.018	0.026	0.956
Pb	0.024	0.057	0.919	0.014	0.019	0.967
Bi	---	---	1.000	---	---	1.000
Th	0.399	0.254	0.347	0.411	0.346	0.243
U	0.237	0.228	0.535	0.206	0.298	0.495

organic fraction of the coal (91,267). The elements are carried from the furnace with the flue gas and deposited on the surface of the fly ash (197,267). The enrichments of Hf and Ta may be caused by their introduction into the flue gas when compounds of other elements which they associate with are vaporized. No elements are enriched significantly in the fly ash-PDC.

The manner in which the amounts of the elements recovered in the total ash are distributed between the three types of ash from the two types of coal is reported in Table V-13. The relative elemental distributions are calculated using:

$$\text{relative distribution}_{B,P,E} = \frac{(0.6,0.34,0.06)\cdot \text{LTA}_{B,P,E}\cdot(B,P,E)}{(0.6\cdot \text{LTA}_B\cdot B)+(0.34\cdot \text{LTA}_P\cdot P)+(0.06\cdot \text{LTA}_E\cdot E)} \quad \text{(V-6)}$$

where the numbers and symbols are the same as in Equation V-3. The elements which form refractory compounds and are associated with the mineral fraction of the coal, such as Be, Ca, Mn, Fe, and S in metal sulfates, have a higher percentage in the bottom ash (i.e., more of the element in the original coal ends up in the bottom ash than in the other two types of ash). More of the volatile and organically associated elements, such as Zn, Ga, Ge, As, Cd, Sb, and Pb, end up in the fly ash-EP. The results reported in Tables V-12 and V-13 indicate that the bottom ash would be a more useful source for the elements which form refractory compounds associated with the mineral fraction of the coal than the other two types of ash. The fly ash-EP would be a more useful source for the elements which are volatile or form volatile compounds

Table V-13. Relative elemental distribution of ashes

Element	Iowa Coal			Colorado Coal		
	Bottom ash (%)	Fly ash PDC (%)	Fly ash EP (%)	Bottom ash (%)	Fly ash PDC (%)	Fly ash EP (%)
Li	60.1	32.5	7.3	71.4	22.3	6.2
Be	72.5	22.4	5.1	84.1	13.3	2.6
B	66.3	27.5	6.2	48.5	40.5	11.0
F	55.1	33.3	11.6	37.7	45.2	17.1
Na	68.3	16.9	14.8	52.8	27.4	19.8
Mg	68.2	21.3	10.4	69.7	24.1	6.2
Al	67.1	24.5	8.4	67.2	27.9	4.9
Si	61.0	35.5	3.5	64.6	31.2	4.2
P	63.8	28,6	7.6	71.7	21.5	6.8
S	79.3	11.4	9.2	87.4	6.1	6.4
Cl	47.8	40.8	11.5	53.3	32.0	14.6
K	58.4	34.8	6.8	72.0	22.2	5.8
Ca	75.2	22.3	2.5	73.4	21.7	4.9
Sc	62.1	27.8	10.1	65.7	28.4	5.9
Ti	57.1	33.6	9.3	76.2	17.0	6.7
V	56.3	29.0	14.8	61.4	30.6	8.0
Cr	62.7	30.3	7.1	62.0	29.2	8.8
Mn	76.8	22.1	1.1	69.2	27.5	3.2
Fe	77.9	18.8	3.4	77.7	21.1	1.2
Co	52.9	31.5	15.7	69.9	20.9	9.2
Ni	65.0	22.7	12.3	67.6	24.0	8.4
Cu	57.7	21.7	20.5	71.1	15.9	13.0
Zn	30.5	21.8	47.6	35.9	18.4	45.7
Ga	32.6	18.7	48.7	35.4	23.5	41.0
Ge	30.5	24.8	44.7	20.1	22.5	57.5
As	20.5	32.2	47.3	10.3	34.9	54.8
Se	71.0	14.8	14.2	69.4	17.3	13.4
Br	65.6	28.9	5.5	72.3	19.8	7.9
Rb	62.4	28.9	8.7	66.4	23.7	9.8
Sr	66.5	22.8	10.7	50.1	39.0	10.9
Y	62.9	25.6	11.4	63.1	31.6	5.3
Zr	62.1	29.6	8.3	57.5	31.1	11.3
Mo	50.4	28.3	21.3	58.6	22.4	19.0
Cd	18.1	16.5	65.4	6.2	20.5	73.4
Sn	56.7	18.4	24.8	23.3	15.2	61.4
Sb	20.3	19.1	60.6	17.0	22.5	60.5
I	38.9	43.7	17.4	20.7	57.0	22.3
Cs	51.5	29.1	19.4	57.6	29.2	13.2
Ba	68.2	21.7	10.2	51.3	39.7	9.0

Table V-13. (Continued)

	Iowa Coal			Colorado Coal		
Element	Bottom ash (%)	Fly ash PDC (%)	Fly ash EP (%)	Bottom ash (%)	Fly ash PDC (%)	Fly ash EP (%)
La	61.3	28.3	10.4	59.1	32.8	8.0
Ce	59.4	28.2	12.5	57.3	33.4	9.2
Pr	60.6	28.2	11.1	61.0	31.8	7.2
Nd	56.3	31.1	12.6	61.8	28.3	9.8
Sm	56.1	31.8	12.0	50.2	38.1	11.7
Eu	64.4	29.3	6.2	56.9	34.8	8.3
Gd	59.6	30.7	9.7	53.1	36.0	10.9
Tb	59.8	34.9	5.2	55.2	35.9	8.9
Dy	59.2	29.1	11.7	47.4	38.8	13.8
Ho	61.9	32.3	5.8	56.4	31.4	12.2
Er	56.3	32.2	11.4	50.4	37.4	12.1
Tm	60.8	30.6	8.6	59.5	31.8	8.7
Yb	51.5	35.6	12.9	51.7	38.9	9.5
Lu	61.9	30.6	7.4	40.7	51.0	8.3
Hf	46.6	41.1	12.3	52.8	28.8	18.5
Ta	69.3	18.6	12.1	70.6	15.6	13.8
W	62.8	26.3	10.9	70.3	17.9	11.8
Hg	74.7	18.0	7.4	65.0	23.4	11.6
Tl	44.0	44.7	11.3	14.2	11.4	74.4
Pb	16.1	21.8	62.0	11.4	8.8	79.7
Bi	---	---	100	---	---	100
Th	69.1	24.9	6.0	65.1	31.1	3.8
U	56.5	30.8	12.8	48.5	39.8	11.7

in the original coal, or are associated with the organic fraction of the coal.

VI. CONCLUSIONS

A calibration scheme which accurately defines the response of the photographic emulsion to the impinging ions from the particular samples of interest is necessary for accurate results using SSMS. The photoplates exposed in this project were calibrated using a computer application of the Franzen-Maurer-Schuy formula. Surprisingly, the results of the calibration indicate an increase in the sensitivity of the emulsion with increasing m/z ratio due to the increasing momentum of the ions.

Of the three internal standards selected for the analysis of the ashed coal and ash samples, Cu, Ba, and Zr, only Cu proved to be suitable for this particular project. The inhomogeneous distribution of Ba in reference and real samples and the difficulty of its dissolution for wet chemical analyses, representing an independent analytical method, precluded its usefulness. The small amounts of sample submitted for wet chemical analysis also precluded the usefulness of Zr as an internal standard because the amounts of Zr in those samples were close to the detection limit (10 μg/50 mL) of the spectrophotometric method (252) employed as another independent analytical method.

The accuracy of the elemental relative sensitivity coefficients is dependent on the accuracy of the elemental concentrations reported for the standard samples. Certified concentrations are best and the rest are suspect in varying degrees according to the homogeneity of the samples, analytical method used, and number of analyses performed. The accuracy of the coefficients is also dependent on the SSMS analyses of the standard samples. It is affected by the homogeneity of the standard samples, position of elemental concentration on the photoplate calibration curve and associated inaccuracies of calibration, number of spectral lines used in the determination of the elemental concentration, and instrumental aberrations.

The precision and apparent accuracy of the relative sensitivity coefficients were found to be satisfactory for the majority of the elements in the standard samples used as cross checks. The large number of standard samples and multiple analyses helped reduce the statistical uncertainty and effect of the systematic errors, but the poor precision (e.g., phosphorous) and small number of concentrations reported for some elements (e.g., rare earths) in the standards increased the inaccuracy of the analytical results for those elements. The precision and apparent accuracy of the elemental concentrations in the Iowa State University Power Plant samples are satisfactory for the majority of the elements. The applicability of the relative sensitivity coefficients to the analyses of these samples may be diminished by differences in the chemical speciation of the elements between the standard and Power Plant samples (262) and the variable response of the SSMS method to elemental differences between the two types of samples due to differences in the handling of the samples (e.g., differences in methods of sample reduction). The results of the analysis of ashed coal and other ashes by SSMS are improved when line areas, instead of peaks, are measured, the mass spectra are interpreted by computer methods, and an accurate calibration and computation scheme with accurate corrections for background fog and other factors is developed.

Results of the material balance study are satisfactory for the majority of the elements studied. They are comparable to results of other similar studies (4,79,262), although this study was more extensive. Systematic errors in relative sensitivity coefficients for specific elements (e.g., phosphorous and the rare earths) account for some of the divergent results while differences in the composition of the three types of Power Plant ash (262) account for others. The uncertainties in the composition of the low-temperature and high-temperature ashes and their distribution also affect the results (266). Nonetheless, the study revealed enrichment of some elements in the three types of ash studied. The bottom ash, which is rich in Be, S, Ca, Mn, and Fe, might be a possible future source of beryllium and manganese. On the other hand, the fly ash from the electrostatic precipitator is relatively rich in Zn, Ga, Ge, As, Cd, Sb, and Pb. As such, it might be a possible source of gallium and germanium which do not exist abundantly in natural deposits. The magnitude of the amount of ash that will result from the burning of coal is so great, however, that it should not be discounted as a future source of valuable materials as other richer sources are depleted.

The ASTM sampling and sample preparation methods provided representative samples, which were important for the success of the material balance study. The inhomogeneity problems found in many aspects of this project may be due to "conglomerates" (273) in the samples. Conglomerates are groups of crystals of different compounds which have grown together simultaneously upon precipitation to form species which are not well defined, but very resistant to crushing by typical grinding methods used in an attempt to homogenize the analytical samples. This resistance and differences in density could have caused some of the elements to be unevenly distributed throughout the samples actually used in the SSMS. The rare earths and other elements (e.g., Zr and Hf) are known to form such species (273). The improved elemental precision and accuracy obtained in this project for the analysis of ashed coal and the products of coal combustion by SSMS indicate that this analytical method is applicable to mass balance studies in coal-fired power plants without requiring sample dissolution which might be a source of contaminants for elements occurring at low levels.

VII. SUGGESTIONS FOR FUTURE WORK

Future research into a number of aspects of this project could improve further the applicability of SSMS to material balance studies in coal-fired power plants. Possible projects include:

1. Further automation of the method to provide more rapid data acquisition and further reduce the total time of analysis could reduce the cost of these studies.

2. Further improvements in sparking stability and reproducibility, further study of the calibration scheme and mass and energy dependence of the emulsion response, and better techniques for sample preparation to improve the homogeneity of the samples could improve further this analytical method.

3. The development of methods to improve the homogeneity of barium in ashed coal and ash samples could make it more useful as an internal standard.

4. Zirconium would be a useful internal standard for samples containing enough of the element to be amenable to cross checking by wet chemical methods of analysis.

5. The suitability of both barium and zirconium as internal standards could be improved by accurate analyses of these elements in ashed coal and ash samples by suitable independent analytical methods other than wet chemical methods (e.g, instrumental neutron activation analysis).

6. The uncertainty in the material balance results could be reduced by collecting separate coal samples at the same time the coal is being used and the ash is being produced and ashing them under conditions similar to those in the furnace to accurately determine the high-temperature ash content.

7. The development of a method of determining the partitioning of the total ash between the various hoppers for the bottom ash, fly ash collected by the primary dust collector, and fly ash collected by the electrostatic precipitator could reduce further the uncertainty in the material balance results.

8. A study of the day-to-day variations in the elemental concentrations of samples collected on different days from the power plant.

9. A material balance study of the coal burned on individual days.

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