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PREPARED FOR THE U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION UNDER CONTRACT AT(07-2)-1

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ABSTRACT

Results of a literature search are presented, and analytical methods are proposed for studies of trace elements in coal, coal ash residue, soil, and vegetation. Increased trace element levels in soils and plants collected near power plants have been reported by several investigators. Many sample dissolution and analysis techniques were used in the reported studies. A nine-laboratory comparison of trace element analyses for a variety of methods showed excessive variation relative to quoted uncertainty limits. Analysis results from a subsequent four-laboratory comparison of instrumental nuclear techniques for trace element analysis agreed with the National Bureau of Standards certified values for all nine elements determined. Instrumental neutron activation analysis, spark source mass spectrometry, and atomic absorption spectrometry are proposed as primary analysis methods for coal, coal ash, soil, and plants in a Savannah River Laboratory study of trace elements. Bomb procedures are proposed for dissolution of samples.

CONTENTS

METHODS FOR ANALYSIS OF TRACE ELEMENTS IN COAL, COAL FLY ASH, SOIL, AND PLANT SAMPLES

INTRODUCTION

Coal contains many metal elements at concentrations ranging from several percent for silicon, aluminum, and iron to a few parts per million or less for other elements. The geology of the coal deposit determines the identity and abundance of the metals in the coal. Wide variations in the chemical composition of coals from different deposits are common.

Combustion converts the organic part of coal to carbon dioxide and water and the nonvolatile inorganic constituents to coal ash residues. About 12% of the coal burned is recoverable as coal ash residues. Coal ash residues consist of approximately 30% bottom ash collected from the bottom of the combustion chamber and approximately 70% fly ash collected from the stack gases by the air pollution control equipment. In the absence of efficient pollution control equipment, fly ash is released to the atmosphere with the stack gases and ultimately settles to the earth.

At the Savannah River Plant (SRP), a 464-MW coal-fired power plant was operated for over 20 years with mechanical collectors to remove fly ash from the stack effluent. Although electrostatic precipitators now remove over 99% of the fly ash from this plant, the mechanical collectors removed only about 75%. During the initial 20 years of operation, an estimated 10,000 to 20,000 tons of fly ash were released to the environment. The cumulative quantities of certain elements emitted in the fly ash may thus be environmentally significant even though they were present at only trace levels in the coal.

The Savannah River Laboratory (SRL) has begun a study[1] to assess the environmental impact of trace metals emitted by the SRP power plant. This study will develop new and improved data on the movement and effects of trace metals in the terrestrial ecosystem surrounding the SRP power plant.

Methods for analysis of selected elements (arsenic, cadmium, chromium, cobalt, copper, lead, manganese, mercury, molybdenum, nickel, selenium, and zinc) are required for this study. To assist SRL chemists in quickly locating significant references applicable to trace element analysis for this study, *Chemical Abstracts* was searched from Volume 82, Number 1 through Volume 83, Number 11.

Abstracts prior to 1975 were not searched because most significant earlier work is referenced by the recent literature. Most research publications written in languages other than English were not read unless the abstract suggested exceptional significance. In addition to the literature search, personnel engaged in trace element analyses at government, university, and private institutions were consulted.

This report documents the literature search and proposes methods for sample dissolution and for analysis of selected elements of interest in coal, coal fly ash, soil, and plant samples.

LITERATURE SEARCH

Analyses of Coal and Coal Fly Ash

Case Studies at Power Plants

A study of trace element paths through a coal-fired power plant was conducted by Oak Ridge National Laboratory at the Tennessee Valley Authority 870-MW Thomas A. Allen Steam Plant in Memphis, Tennessee. In-plant samples[2] were analyzed to determine emission characteristics[3,4] and to obtain mass balances[5-8] for 37 elements. They concluded that Hg, Se, and probably Cl and Br were discharged to the atmosphere as gases. Some elements (As, Cd, Cu, Ga, Mo, Pb, Sb, Se, and Zn) were substantially more concentrated in fly ash than in slag. Other elements (Cr, Na, Ni, Sc, U, and V) were moderately more concentrated in fly ash than in slag, but several elements (Al, Ba, Ca, Ce, Co, Eu, Fe, Hg, K, La, Mg, Mn, Rb, Si, Sm, Sr, Ta, Th, and Ti) exhibited little preferential partitioning.

Although the Oak Ridge - Allen Plant study is the most comprehensive, other studies of trace elements in coal-fired power plants have been reported. The University of Colorado[9] determined mass balances for 16 elements at the 180-MW Valmont Power Plant near Boulder, Colorado. The U.S. Bureau of Mines[10] studied the fates of Hg, Cd, and Pb during coal combustion in a 100 g/hr combustor, in a 500 lb/hr furnace, and in commercial power plants. The Bureau of Mines also investigated the distribution of Cr, Cu, F, Hg, Mn, and Ni in coal with specific gravity separations to divide the coal into discrete fractions.

Analytical Methods

Many analytical techniques were used in the power plant studies. Those techniques used by Oak Ridge at the Allen Plant are best described in the Otaniemi Symposium Proceedings[11] and in one progress report.[2] The Oak Ridge study relied primarily on neutron activation analysis (NAA), spark source mass spectrometry (SSMS), and atomic absorption spectrometry (AAS) for most bulk analyses. Fly ash particle characterization by scanning electron microscopy, x-ray fluorescence spectrometry, and x-ray photoelectron spectrometry is described in References 3 and 4.

The analytical techniques used in the University of Colorado study at the Valmont Plant are thoroughly documented.[9] Sample collection, preparation, and analysis are described; precision and errors are discussed; and conclusions and recommendations are given. The University of Colorado used primarily wet chemical methods, AAS, and x-ray fluorescence spectrometry to determine elemental concentrations for this study. The Bureau of Mines used AAS for analysis of all metal elements. Standard materials were not available as references; therefore, the method of standard additions was used to eliminate matrix effects.

Methods for determination of trace elements in coal[12-16] and fly ash[17] have been reported by others not specifically engaged in power plant studies. In addition, the book edited by Babu[18] is devoted entirely to the analysis of trace elements in fuels and contains chapters by prominent scientists describing various analytical techniques.

Interlaboratory Comparison of Analytical Methods

Three programs have been conducted to compare interlaboratory results for analysis of trace elements in coal and fly ash. The first[19] was initiated by the Environmental Protection Agency (EPA). Nine laboratories with in-depth analytical experience in the determination of trace environmental materials were asked to determine the concentrations of 28 elements in the same samples of coal, fly ash, fuel oil, and gasoline by each of six EPA-specified methods. The results for most elements from the participating laboratories showed enormous variation far in excess of the quoted limits of uncertainty. Agreement was within an order of magnitude in all four matrices for only seven of the 28 elements. The variation was attributed primarily to sample preparation, interferences peculiar to the analysis methods, or operator error. Although some sample inhomogeneity was suggested by the range of iron concentrations, inhomogeneity could account for only a moderate portion of the large variation.

The second interlaboratory analysis comparison[20] was conducted by four laboratories by instrumental neutron activation analysis, instrumental photon activation analysis, or direct gamma counting to analyze for 37 elements in National Bureau of Standards (NBS) standard coal (SRM 1632) and for 41 elements in NBS standard fly ash (SRM 1633). The generally excellent agreement among the four participating laboratories with instrumental nuclear techniques was in sharp contrast to the poor agreement obtained in the earlier nine-laboratory study.[19] Within the limits of error, the interlaboratory mean agreed with the NBS value for all nine certified elements in fly ash and for nine of the ten certified elements in coal. The four laboratories did not report analyses for lead in coal, the tenth NBS-certified element.

The precision (relative standard deviation) of the interlaboratory data was calculated for all elements with two or more reported values. Of the 30 elements meeting this criterion in coal, the relative standard deviation did not exceed 10% for 17 elements, did not exceed 15% for 25 elements, and did not exceed 25% for all 30 elements. Elemental analyses of fly ash were not as precise as those of coal. For 30 elements in fly ash, the relative standard deviation did not exceed 10% for 16 elements and did not exceed 15% for 26 elements, but two values (W and Yb) were 25% or greater. In cases where comparisons could be made, both the accuracy and interlaboratory dispersion of results obtained in the analysis of coal and fly ash by nuclear methods were generally superior to those reported in the nine-laboratory comparison by six EPA-specified methods. This was attributed to the fact that virtually no pretreatment of samples is necessary for the nuclear activation methods.

The third interlaboratory comparison[21] concentrated efforts of approximately 60 laboratories on the analysis of 15 elements (As, Be, Cd, Cr, F, Hg, Mn, Ni, P, Pb, S, Se, U, V, Zn) in coal, fly ash, fuel oil, and gasoline. These unpublished data give all experimental analyses listed by element with method and laboratory number identified. Statistical parameters (including accuracy, range, and precision) are presented for analysis of each element by each method in each matrix.

Analyses of Soil and Plants

Case Studies

Studies to relate the emissions from fossil fuel combustion to the trace element content of surrounding soil and plants have been conducted. Klein and Russell[22] reported enrichment of Ag, Cd, Co, Cr, Cu, Fe, Hg, Ni, Ti, and Zn in soil and Cd, Fe, Ni, and Zn in plants collected around a 650-MW power plant near Holland, Michigan. Enrichment was confined to the upper two centimeters of soil and correlates well with wind patterns and the metal content of coal for each element except mercury, which was only slightly enriched.

The Oak Ridge - Allen Plant study investigated also major and minor elements[4] in soil and in moss (Dicranum) samples collected along a 40-mile transect through the plant. The concentrations of most major elements (Al, Ca, Fe, Mg, Mn, Na, and Ti) in soil varied by approximately a factor of two over the sampled area.[2] The concentrations of some minor elements in the upper one centimeter of soil also varied considerably; whereas for others, the concentrations varied only slightly. Soil samples collected under trees generally contained higher concentrations of trace elements than samples collected in open areas. The analytical data for soil indicated no accumulation of trace elements that could be attributed to the power plant. Trace element concentrations in moss were uniformly lower than in the surrounding soil.

Other studies of trace elements in soil and plants were not directly related to fuel combustion. Klein[23] analyzed soil samples from a 300 square mile area enclosing metropolitan Grand Rapids, Michigan, and found higher concentrations of several metals (Ag, Ca, Cd, Co, Cr, Cu, Fe, Ni, Pb, and Zn) in industrial areas than in residential and agricultural areas.

Poelstra[24] studied the behavior of mercury compounds in 15 different European soils. Mercury and its compounds were strongly adsorbed in the top layer of soil. Leaching of mercury is minimal. Evaporation of dimethyl mercury from soil occurs at a high rate, but for most other mercury compounds the evaporation rate is probably low.

Peyton and McIntosh[25] reported elevated levels of cadmium, zinc, and lead in soil from a borrow pit and in sediment from a small pond both near the Indiana Toll Road. Cadmium-lead-zinc ratios suggest that steel-making processes contribute to the metal content of the borrow pit; whereas, automobile exhaust emissions are responsible for the high lead content of the pond sediments. Initial AAS data indicate a correlation between percent organic matter and heavy metal content.

Benenati[26] used AAS to study the concentrations and distributions of zinc, lead, cadmium, and arsenic in soil, vegetation, and water resources sampled within a 7-mile radius of the zinc smelter in Blackwell, Oklahoma. Within a pasture adjacent to the smelter he found that decreased productivity, altered floristic composition, and lowered species diversity correlated with increased proximity to the smelter and increased levels of metals in both soil and vegetation.

Analytical Methods

Methods for analysis of trace elements in soil and plants have been developed, improved, or evaluated by many researchers. Nadkarni[27] demonstrated the applicability of NAA to biomedical and environmental studies by analyzing soil, plant, and animal tissue samples for 29 elements.

Jervis[28] applied a neutron activation procedure based on radiochemical isolation of ^{115}Cd to analyze for cadmium at the parts per billion level in foods, vegetables, and hair. He used an instrumental photon activation method (15 or 35 MeV) with assay of ^{111m}Cd to analyze soil, fertilizer, and a few vegetation samples at parts per million levels. Jervis noted that cadmium and zinc tend to occur together and to concentrate in organic matter in soils.

Very low detection limits are frequently reported for NAA. Chemical separations may be required to achieve these levels in biological samples because bulk elements with appreciable cross sections may interfere. Spyrou et al.[29] discussed this limitation and presented realistic detection limits for neutron activation analysis of biological samples.

A method for determining molybdenum in plants by NAA was developed by Singh and Steinnes.[30] This method requires wet ashing of irradiated samples in H_2SO_4/H_2O_2 and quantitative separation of the induced ^{99}Mo activity on an anion exchange resin.

Bradfield and Stickland[31] developed an AutoAnalyzer* method for the analysis of molybdenum in plants. The method is based on the catalytic effect of molybdenum on the liberation of iodine from the reaction between potassium iodide and hydrogen peroxide. The detection limit for molybdenum is 0.003 μg/ml.

Haddad[32] developed interference-free methods for determination of molybdenum in soils and in plants with detection limits of 0.1 and 0.05 μg, respectively. The method for soils is based on spectrophotometric determination of a molybdenum oxypentathiocyanate-rhodamine B complex. The method for plants is based on extinction of rhodamine B fluorescence by complex formation.

A revised procedure for extracting molybdenum from soil with an anion exchange resin (before analysis by the spectrophotometric thiocyanate procedure[33]) and a method for eliminating colorimetric interferences of soluble organic matter from the extracts are reported by Jackson and Meglen.[34]

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* Trademark of Technicon Controls, Inc.

A critical examination of the 2,3-diaminonaphthalene fluorometric method for determination of selenium in plants is given by Haddad and Smythe.[35]

The use of inductively coupled plasmas as spectrometric emission sources for the determination of iron, manganese, copper, aluminum, boron, and zinc in orchard leaves was reported by Scott and Strasheim.[36]

The determination of low concentrations of copper in small (100-500 mg) samples of plant material by AAS with a heated graphite atomizer was investigated by Simmons and Loneragan.[37]

Bergseth[38] demonstrated the applicability of a modified background-ratio method to the direct x-ray fluorescence determination of zinc in soil samples containing different amounts of organic matter. Results correlated well with those obtained by AAS.

A simple method for determining uranium in soil by a two-stage ion exchange separation followed by alpha counting was reported by Baltakmens.[39] McDowell[40] thoroughly investigated a high-resolution liquid scintillation-solvent extraction method for uranium and plutonium analyses that is applicable to typical environmental soil leach and waste water samples.

The efforts of the NBS to prepare, analyze, and market standard reference materials for determination of trace elements in environmental samples were described by LaFleur.[41] Laitinen[42] discussed general considerations relevant to the chemical analysis in environmental research of air, water, soil, plants, and animals.

Literature Reviews of Analytical Methods

In addition to research reports, comprehensive literature reviews have been published. Hattman, Schultz, and Smith[43] surveyed methods of sampling, analyzing, and testing solid and gaseous fuels. Dinnin[44] reviewed recently published analytical methods applicable to inorganic and geological materials. Straub and Hurwitz[45] reviewed elemental analytical methods for ferrous metals; Seim, Calkins, and Macksey[46] reviewed nonferrous metallurgical analyses. These well-organized and extensively documented reviews provide ready references for specific analyses required during this SRL study.

PROPOSED ANALYTICAL METHODS

Instrumental neutron activation analysis, spark source mass spectrometry, and atomic absorption spectrometry are proposed for analysis of coal, coal fly ash, soil, and plant samples. Table 1 summarizes the proposed methods for each element. These methods have been extensively evaluated for environmental trace element studies, and their applicability has been documented in recent literature. The precision and accuracy of each method have been demonstrated[20,21] for many elements in several NBS-certified environmental standards by comparing analysis results from 60 laboratories.

Instrumental Neutron Activation Analysis (INAA)

INAA is an excellent method for the analysis of environmental samples because it is rapid, highly sensitive, does not require sample dissolution, and is relatively free of matrix interferences. Direct analysis with minimum sample handling is desirable not only for economic reasons, but also because it reduces the probability of sample contamination and loss of volatile elements. INAA analyzes large quantities (several grams) of each sample and thus minimizes inhomogeneity effects. Several elements cannot be determined by INAA. This method is useful only for elements which, upon activation, produce radioactive isotopes giving statistically significant decay signals.

Spark Source Mass Spectrometry (SSMS)

SSMS is a rapid multielement technique with minimal matrix effects. It is capable of simultaneously determining all elements of interest in this study. SSMS complements INAA by providing analytical capability for several elements (Cd, Cu, Hg, Ni, Pb, Zn) not readily determined by INAA; in addition, it provides a check for INAA results for the remaining elements (As, Co, Cr, Mn, Mo, Se). SSMS permits analysis without sample dissolution, thereby minimizing sample preparation time and reducing the probability of contamination or constituent loss. The precision of a general scan analysis is poor (±50%).[2] For increased precision, isotope-dilution spark source mass spectrometry (IDSSMS) can be applied to the analysis of many elements to give ±3% precision.[2] It is normally advisable to dissolve samples for IDSSMS to assure isotope equilibrium during analysis. SSMS analyzes extremely small samples, and for certain applications it offers distinct advantages over other techniques. The analysis of such small samples, however, tends to enhance inhomogeneity effects.

Atomic Absorption Spectrometry (AAS)

AAS is an accurate and precise analysis method. Although it was initially limited to analysis of certain elements in water solution, its applicability has been extended by technical developments to include all of the elements of interest in this study. As outlined by Pollock,[47] the atomic absorption analyses can be divided into four groups: elements that can be determined by conventional flame analysis (Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn); elements that can be determined by flameless AAS with a graphite furnace (As, Cd, Cr, Pb, Zn); elements that can be determined by evolution of their volatile hydrides (As, Se); and a miscellaneous group that requires special methods (Hg, Se).

The graphite furnace method provides greater sensitivity than conventional flame procedures and greater convenience than hydride volatilization procedures. The Hatch and Ott[48] cold vapor method has proved highly sensitive and very reliable for mercury analysis. Selenium can be analyzed by the graphite furnace method[49] used extensively at the Cincinnati EPA laboratory or by a hydride evolution method.[50]

A colorimetric[31-33] or fluorometric[32] method is proposed as the third technique for molybdenum analysis because either offers excellent sensitivity and is less subject to interferences than AAS.[51]

TABLE 1. Summary of Proposed Methods

	Method in Preferred Order		
Element	*First*	*Second*	*Third*
As	INAA	SSMS	AAS^{a}
Cd	SSMS^{b}	AAS^{c}	
Co	INAA	SSMS	AAS^{c}
Cr	INAA	SSMS	AAS^{c,d}
Cu	SSMS^{b}	AAS^{c}	
Hg	SSMS^{b}	AAS^{e}	
Mn	INAA	SSMS	AAS^{c}
Mo	INAA	SSMS	COLOR
Ni	SSMS	AAS^{c}	
Pb	SSMS^{b}	AAS^{c,d}	
Se	INAA	SSMS	AAS^{d}
Zn	SSMS^{b}	AAS^{c,d}	

INAA - instrumental neutron activation analysis
SSMS - spark source mass spectrometry
AAS - atomic absorption spectrometry
COLOR- colorimetric thiocyanate or equivalent

a. Hydride evolution
b. Isotope dilution
c. Conventional direct flame
d. Graphite furnace
e. Hatch and Ott

SAMPLE COLLECTION AND PREPARATION

Sample collection sites have been evaluated to define trace element paths through the SRP power plant. These paths can be quantitatively defined from experimental mass flow rates and elemental analysis data for the following samples:

- Coal sampled at the combustion chamber inlet
- Slag from the combustion chamber
- Material (solid and gaseous) entering the electrostatic precipitator
- Material collected by the electrostatic precipitator
- Material (solid and gaseous) emitted from the power plant stack

Data for the first three samples are sufficient to permit mass balance calculations, but data for all five samples are required to calculate mass balances and define metal emissions accurately. It is therefore proposed that all five sample types be collected by standard methods[52] to assure representative and reproducible samples.

Sample preparation is a critical step in any trace analysis. Although different sample preparations may be required for each sample type and for each method, all methods used in this study for analysis of solid samples have a common denominator. All relate analytical results to the weight of the dried sample. It is therefore proposed that all solid samples be dried, ground, and sieved in one facility. A standard method[53] should be used to ensure comparable dry weights for each analytical method, to reduce sample inhomogeneities, and to provide samples with more uniform digestion characteristics.

SAMPLE DISSOLUTION

Sample dissolution is required for analysis by AAS and by wet chemical methods and may be required for IDSSMS. No single technique is equally satisfactory for dissolution of all samples. Plant material and coal require dissolution techniques capable of decomposing large quantities of organic material. Coal slag and fly ash require techniques capable of dissolving acid-resistant minerals and glasses. Soil may require an intermediate technique depending on mineral and organic content.

The Bernas[54] procedure is proposed for dissolution of slag, fly ash, and soils with very low organic content. Silicates are decomposed in 30 to 40 minutes at 110°C without volatilization losses in a specially designed vessel lined with polytetrafluoroethylene (commonly known as a Parr bomb[55]). The decomposition medium of hydrofluoric acid, boric acid, and aqua regia provides a salt-free matrix that offers negligible interference during atomic absorption analysis. The Bernas procedure permits volume measurements in calibrated glass containers, but does not introduce metallic cations to the solution. This dissolution procedure has been satisfactorily applied[54-57] to the atomic absorption analysis of 18 metallic elements in rock and sediment samples. The Bernas dissolution procedure may be applicable to the atomic absorption analysis of arsenic, selenium, cadmium, and mercury. Although no literature reports were found that describe this application, Pollock[47] used hydrofluoric acid dissolution for both graphite furnace and hydride volatilization analyses for arsenic. The applicability of the Bernas dissolution technique for the colorimetric or fluorometric analysis of molybdenum is uncertain.

For analysis of soil samples containing substantial amounts of organic matter and for analysis of volatile elements in plant and coal samples, the Hartstein[58] modification of the Bernas procedure is proposed for sample dissolution. Fuming nitric acid is used to decompose organic matter in the bomb before addition of hydrofluoric and boric acids. Hartstein demonstrated the applicability of the modified procedure for atomic absorption analysis of ten metallic elements in coal. This modified Bernas procedure has also been used by SRL to dissolve coal samples for mercury analysis by the Hatch and Ott cold vapor method.

For dissolution of plant samples, the high-temperature ashing procedure and the nitric acid — perchloric acid digestion procedure of Isaac and Johnson[59] are proposed. Seven laboratories participated in a collaborative study to compare these procedures for analysis of several metallic elements in plants. They found both dissolution procedures equivalent and acceptable.

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