

**INORGANICS IN FUEL:  
A CENTURY OF SCIENTIFIC AND ENGINEERING PROGRESS**

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**INTRODUCTION**

Combustion of fossil fuels has been the backbone of the power generation, manufacturing and transportation industries in the twentieth century. Although the mix of fuels has changed, at the close of the century we find that combustion systems have not changed overmuch. Operational caused by inorganic elements in fossil fuels (corrosion, slagging, and fouling) continue to present problems in combustion systems, although substantial progress has been made in understanding and addressing such problems. In the latter half of the century, the impact of inorganic elements in fossil fuels on the environment was recognized as a potential problem. Considerable effort has therefore been directed at understanding the behavior of certain trace metals such as mercury, arsenic, nickel, chromium, and selenium during the combustion process. This paper briefly reviews the behavior of inorganic elements in practical combustion systems as well as the progress made in applying this knowledge to improvements in operational and environmental performance.

Most inorganic elements in the periodic table can be found in fossil fuels, although only a small number occur in significant concentrations to cause operational or environmental problems. Coal has by far the highest content of ash, although the chemical composition of lower ash fuels can make oil and biomass problematic in some instances. Table 1, drawn largely from Bryers,<sup>1</sup> summarizes the contributions of the elements in ash from various fuels to slagging, fouling, corrosion, and environmental problems. Slagging is defined as deposition of fly ash in the radiant section of the furnace, on both heat transfer surfaces and refractory surfaces. Fouling occurs in the convective heat transfer section and includes deposition of ash and volatiles as well as sulfidation reactions of ash. Fouling results in loss of heat transfer efficiency and blockage of the gas flow path. Corrosion occurs primarily on the water-wall tubes in the radiant section of the boiler and results in thinning of tubes with eventual leaks.

Table 1. Impact of Inorganic Elements in Fuel on Operational and Environmental Problems.

	<i>Bituminous Coal</i>	<i>Subbituminous Coal</i>	<i>Lignite</i>	<i>Oil and Coke</i>	<i>Biomass</i>
<b>Wt% Ash</b>	5-20%	4-7%	5-20%	0.1-0.5%	1-3%
<b>Si</b>	S		S		S
<b>Al</b>	S		S		
<b>Fe</b>	S		S		
<b>Mg</b>	S		S		
<b>Ca</b>	S	F, S	F, S		
<b>Na</b>	C, F	F	F	F, C	C, F
<b>K</b>	S				C, F
<b>S</b>	C, F	F	F	C, F	C, F
<b>Cl</b>	C				C
<b>Ni</b>				F	
<b>V</b>				C, F	
<b>As</b>	E	E	E	E	
<b>Cr</b>				E	
<b>Hg</b>	E	E	E	E	

Major elements are shown in **bold**

C - Corrosion  
E - Environmental  
F - Fouling  
S - Slagging

Environmental problems include the impact of ash on the air pollution control devices (APCDs) and on the environment. Increasingly, the emission of toxic metals to the air and water from fossil fuel combustion is recognized as a problem. Mercury is the element of most concern, particularly for coal-fired power plants. Other metals (e.g., As, Cr, Ni, V) are also of concern when burning petroleum-derived fuels. There are other impacts of inorganic elements in the environmental performance of combustion systems, including operation of particulate collection

devices and the poisoning of selective catalytic reduction catalysts by arsenic. In coal-fired power plants, the sodium and sulfur contents of the fuel both affect the resistivity of the fly ash. If an electrostatic precipitator (ESP) is used to collect the ash, resistivity is the key ash parameter which influences the collection efficiency.

## CHARACTERIZATION OF INORGANIC ELEMENTS IN FUEL

Coal was the first fossil fuel to be used for generation of steam applied to transportation and manufacturing, and later to large-scale power generation. Heavy oils and coke, produced from refining of petroleum have been utilized for power generation and manufacturing in the latter half of the century. Wood and agricultural wastes (biomass) have been used at a low level throughout the century, and this may increase with concerns about the use of non-renewable resources. Most of the fossil fuels used for large scale industrial use have a substantial fraction of inorganic elements, the exceptions being natural gas and transportation fuels such as gasoline and diesel oil.

Early methods for characterizing inorganic elements in coal were indirect, for example, ash content or fusibility of the ash. It acknowledged early on that the composition of coal ash strongly influenced the tendency to form deposits in the combustion system. Beginning in the 1930's, the contribution of specific minerals to slagging and fouling problems was recognized using methods of density separation to isolate mineral-rich fractions of coal.<sup>2</sup> With the advent of cyclone boilers for pulverized coal, viscosity measurements were made on coal ash.<sup>3</sup> Mineralogical characterization of coal continued, resulting in a fairly comprehensive understanding of the occurrence and formation of the major minerals in coal by techniques such as physical separation, selective leaching, and x-ray diffraction analysis. Table 2 summarizes the important minerals in coal.<sup>1</sup> More recently, automated techniques such as computer controlled scanning electron microscopy (CCSEM)<sup>4</sup> and scanning electron microscopy point count (SEMPIC)<sup>5</sup> have been developed to provide a more accurate picture of the minerals in coal.

Table 2. Minerals occurring in coal

Quartz
Shale group
Species: illite, montmorillonite, muscovite, bravaisite
General formula: $(K, Na, H_3O, Ca)_2 (Al, Mg, Fe, Ti)_4 (AlSiO_8O_{20}(OH,F)_4)$
Kaolin group
Species: kaolinite, livesite, metahalloysite
Formula: $Al_2(Si_2O_5)(OH)_4$
Sulphide group
Species: pyrites, marcasite
Formula: $FeS_2$
Carbonate group
Species: calcite, dolomite, ankerite
Formula: $(Ca, Mg, Fe, Mn) CO_3$
Chloride Group
Species: sylvite, hallite
Formula: $KCl, NaCl$

Since the 1960's, low rank coals have become more widely used for steam generation because of their low ash and sulfur contents. Low rank fuels have a major proportion of inorganic elements organically bound to the coal matrix instead of in discrete minerals. Selective leaching (or chemical fractionation) methods have been used to identify and characterize the organically bound elements, primarily Ca, Na, and Mg in subbituminous and lignite coals.<sup>6</sup> Recently, selective leaching and advanced analytical methods such as X-Ray absorption fine structure spectroscopy have been applied to the problem of determining the forms of occurrence of trace elements in coal.<sup>7,8</sup>

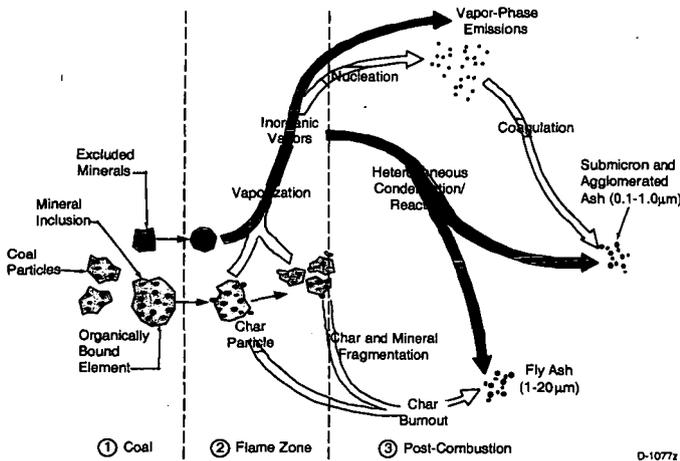
Oil and coke, as well as biomass, have much lower ash contents than coal and little, if any minerals (although the inorganic elements in these fuels can still cause problems in practical combustion systems). Generally the ash content and ash composition of these fuels is all that is measured, although the mineralogy and leaching behavior of elements of some biomass fuels have been reported.<sup>1</sup>

## IMPACT OF INORGANIC ELEMENTS ON SYSTEM OPERATION

At the start of the twentieth century, coal burned in stoker-fired units was the most common for industrial applications. In the 1920's pulverized coal was introduced and this allowed the design and implementation of new combustion system designs, including wall-fired boilers, cyclone boilers, and fluidized bed combustors. Large scale refining of petroleum in the latter half of the twentieth century introduced new fuels, heavy oils and coke, which are often burned to produce steam and/or electricity in suspension-fired and fluidized bed combustion systems.

Figure 1 illustrates the transformation of inorganic elements during coal combustion. Petroleum-derived fuels and biomass transformations are similar, although these fuels have less discrete mineral matter than coal. During the combustion process, the carbon matrix is consumed resulting in very high particle temperatures. Most of the inorganic elements (either from discrete minerals or organically associated) coalesce into ash particles in the range of 1-20 microns in diameter. A small part of the inorganic elements vaporize during the combustion process (1-5 wt%) and recondense, forming a fine (0.1-0.5 micron) aerosol. Some inorganic vapors condense on the larger ash particles, but the high specific surface area of the submicron aerosol tends to bias condensation to the smaller particles.

These ash particles reside largely in the flue gas in pulverized coal- or oil-fired combustion systems. In cyclone-fired boilers and fluidized bed systems, the majority of the ash ends up as slag or spent bed material. This fly ash, in the flue gas, deposits on heat transfer surfaces in the boiler and ultimately, on modern coal-fired combustion systems, must be removed before the gas can be emitted to the atmosphere.



**Figure 1. Transformations of Inorganic Elements During Combustion of Pulverized Coal**

As discussed above, slagging, fouling and corrosion affect the operation of industrial combustion systems and are directly caused by inorganic elements in fossil fuels. Coal combustion systems are plagued by all these problems. Corrosion is the dominant problem in oil-fired boilers because of the formation of vanadium sulfate deposits which are quite corrosive. Corrosion can be a problem in some biomass combustion systems because some biomass fuels have a very high alkali content. The combination of silica and alkali can also result in slagging and fouling.

Initially, empirical indices were developed to evaluate the potential for operational problems due to the inorganics in fuels. There are many such indices,<sup>1</sup> but they are not specific to particular boiler designs or operating conditions. As discussed above, the realization that specific minerals in coal were responsible for slagging, fouling, and corrosion led to an explosion of research on mineralogical characterization of fuels. This was followed by attempts to create mechanistic (as opposed to empirical) models for the behavior of inorganic elements in practical combustion systems.<sup>9,10,11</sup> Such models are used to provide better indications of the potential effects of fuels on system operations.

## IMPACT OF INORGANIC ELEMENTS ON THE ENVIRONMENT

The emission of toxic metals to the air and water from fossil fuel combustion is becoming of concern. In the United States, the potential for regulation of hazardous air pollutants, including metals, was specifically addressed in the 1990 Amendments to the Clean Air Act.

A recent report by the Environmental Protection Agency (EPA) on emission of hazardous air pollutants by electric utilities predicted that emissions of air toxics from coal-fired utilities would increase by 10 to 30% by the year 2010.<sup>12</sup> Mercury from coal-fired utilities was identified as the hazardous air pollutant of greatest potential public health concern. Anthropogenic emissions of mercury account for 10 to 30% of the world-wide emissions of mercury.<sup>12</sup> EPA has estimated that during the period 1994-1995 annual emissions of mercury from human activities in the United States were 159 tons.<sup>12</sup> Approximately 87% of these emissions were from combustion sources. Coal-fired utilities in the U.S. were estimated to emit 51 tons of mercury per year into the air during this period. Considerable work is in progress by the author,<sup>13</sup> and many other groups, which will lead to a more complete understanding of the behavior of mercury in coal-fired power plants.

Other metals (e.g., As, Cr, Ni, V) are also of concern when burning petroleum-derived fuels. Chromium and nickel are the metals of most concern for residual oil combustion. Certain compounds of Cr and Ni are highly carcinogenic. Advanced analytical methods such as XAFS have been used to identify compounds of these elements in residual oil fly ash in order to assess the potential health risks.<sup>14</sup> Cd and Zn in biomass fly ash have also been characterized by this technique. When considering the potential risk to human health or to the biosphere, the ability to identify specific compounds of these toxic metals becomes vitally important. Advanced analytical methods have proved useful in the past and are continually being improved.

### SUMMARY

Inorganic elements are present in almost all industrially important fossil fuels and can have major impacts on operation and environmental performance of fossil fuel combustion systems. Improved analytical methods for measuring the composition and for characterizing the form of inorganic elements in fuels have been developed. These methods have led to a better understanding of the behavior of inorganic elements in combustion systems and have spurred the development of fundamentally based models which have been applied in practical systems. More recently, concerns have been raised over the impact of fossil fuel combustion systems on the environment. Advanced analytical methods are just now starting to be applied to characterization of trace metals in fossil fuel and in combustion byproducts. This will lead to an improved understanding of the behavior of trace metals in combustion systems and more effective methods to assess the potential risk to human health.

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# MODES OF OCCURRENCE OF TRACE ELEMENTS IN COAL: RESULTS FROM AN INTERNATIONAL COLLABORATIVE PROGRAMME

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## INTRODUCTION

A collaborative research project on the modes of occurrence of trace elements in coal was set up within the IEA implementing agreement on Coal Combustion Sciences. Les Dale of CSIRO, Australia, coordinated the project. Participants in the project were requested to determine the modes of occurrence of trace elements of environmental significance using their chosen methodology. The aim was to determine not only the modes of occurrence but also to obtain data that could be compared and contrasted. The final reports were then sent to IEA Coal Research to form the basis of a critical review of the project (Davidson, 2000). They have been published on the CD-ROM that accompanies the overall final report.

The collaborative programme was set up because the participants believe that understanding the modes of occurrence in coal is essential for developing reliable models to predict the behaviour of elements during in-ground leaching, weathering, coal cleaning, or combustion. Modelling the behaviour of the trace elements is necessary to provide an accurate evaluation of the environmental and human health impacts, technological impacts, and economic by-product potential of coal use (Willett and others, 2000). Knowledge of the mineralogical residences or modes of occurrence of trace elements in coal is very important in the understanding of mechanisms by which trace elements are enriched in fly ash and are found in flue gas (Dale and Chapman, 1999). This is because the behaviour of the trace elements in coal-fired power stations is partly dependent on the mode of occurrence of the elements in the original coal (Wigley and others, 2000).

## THE PARTICIPATING LABORATORIES

Laboratories in Australia, Canada, Spain, the United Kingdom, and the USA participated in the collaborative study:

Australia	CSIRO, Division of Energy Technology, Lucas Heights, NSW (Dale and Chapman, 1999)
Canada	Geological Survey of Canada, Energy and Environment Division, Calgary, Alberta (Goodarzi and others, 1999).
Spain	Institute of Earth Sciences "Jaume Almera", CSIC, Barcelona (Querol and others, 1999)
UK	University of Sheffield, Centre for Analytical Sciences, Sheffield (Spears and others, 1998)
UK	Imperial College of Science, Technology and Medicine, Department of Materials, London (Wigley and others, 2000)
USA	Energy & Environmental Research Center, University of North Dakota, Grand Forks, ND (Galbreath and others, 1999)
USA	University of Kentucky, Department of Chemical and Materials Engineering, Lexington, KY (Huggins, 1999)
USA	US Geological Survey, Reston, VA (Willett and others, 2000)

## THE COALS SELECTED

In the initial stages of the project, three different coal samples were distributed. A fourth coal, from a mine in Nova Scotia, Eastern Canada was distributed to participants about a year after the first three coals were distributed. Not all the collaborating laboratories were able to study all four samples, but most were able to study the Australian, British, and US samples. The coals selected were:

- Wyee coal - a high volatile bituminous Australian coal,
- Gascoigne Wood - a UK bituminous coal from a 2 tonne batch from power station feed,
- Illinois No. 6 - a high volatile US bituminous coal, and an
- Eastern Canadian coal - also high volatile bituminous.

Table 1 lists some analytical data provided by Goodarzi and others (1999).

**Table 1 Proximate and ultimate analyses of the four coals (Goodarzi and others, 1999)**

	Wye, Australia	Eastern Canadian	Gascoigne Wood, UK	Illinois No. 6, US
Proximate analysis, wt% ar				
Moisture	2.6	1.33	3.2	3.3
Ash	23.0	9.86	15.2	10.1
Volatile matter	27.1	31.96	29.6	36.1
Total sulphur	0.37	3	1.16	3.4
Ultimate analysis, wt% daf				
Carbon	63.62	75.31	69.2	69.84
Nitrogen	1.31	1.38	1.58	1.36
Sulphur	0.38	3.00	1.20	3.52
Hydrogen	3.46	4.53	4.03	4.27
Oxygen	7.62	6.12	8.25	10.57
Sulphur forms, wt%				
Sulphate S	0.01	0.30	0.08	0.08
Pyritic S	0.05	1.70	0.32	1.30
Organic S	0.31	1.00	0.76	2.02

**MINERALOGY**

Goodarzi and others (1999) provide a comprehensive account of the mineralogies of the coals used in these studies. Most of the collaborating laboratories analysed the mineral composition of the coals although different methods were used. The analyses of the bulk ash contents are in reasonably close agreement for all the laboratories that provided data. However, some differences emerge in the detailed data. Huggins (1999) reports values for the float/tailings fractions and their ash content for separations performed using a Denver flotation cell. Galbreath and others (1999) separated the coals using a 1.6 specific gravity solution for the Wye coal and a 1.45 specific gravity solution for the other three. The data are compared in Table 2 that lists the percentage ash remaining in each fraction.

**Table 2 Percentage ash separation analyses (Galbreath and others, 1999; Huggins, 1999)**

	Wye, Australia	Eastern Canadian	Gascoigne Wood, UK	Illinois No. 6, US
Density sink	73	76	73	54
Denver cell tailings	40	49	69	21
Density float	27	24	27	46
Denver cell float	60	51	31	79

The differences, except for the Gascoigne Wood coal, are considerable but most likely reflect physical differences in the separation methods. The differences in the separations by different mechanical separations could possibly lead to different assignments of the trace element modes of occurrence. It would be expected that a greater proportion of trace elements will be found in the maceral-rich fraction from Denver cell flotation except, possibly, for the Gascoigne Wood coal. Although, when at least 24% of the ash is encountered within the maceral-rich float fractions, this is scarcely evidence for 'maceral-association' rather than 'mineral-association' with minerals dispersed within the bulk of the organic matter. Galbreath and others (1999) observed that most of the minerals in their float fractions were present as tiny (< 5 µm in the longest dimension) inclusions within coal particles. Most of the trace elements are enriched to some extent in the tailings fractions (Goodarzi and others, 1999) but, even when depleted in the float compared with the coal, a greater proportion of the trace elements often remains there.

**THE TRACE ELEMENTS COMPARED**

Not every trace element was analysed by every laboratory so that comparisons among them have to be made using a restricted set. The eleven elements identified in the US Clean Air Act Amendments (CAAA) of 1990 as potentially 'hazardous air pollutants' with the addition of copper and zinc formed the basis of the overview report:

**Beryllium, chromium, manganese, cobalt, nickel, copper, zinc, arsenic, selenium, cadmium, antimony, mercury, and lead.**

A range of analytical techniques was employed in the qualitative and quantitative analysis of the elements in the coals and their fractions. Generally, the data for the concentrations of these trace elements in the whole coal were in reasonably good agreement

### **SAMPLE FRACTIONATION**

In order to determine the modes of occurrence of the trace elements in the samples, the coals were fractionated using variants of two techniques - **physical separation** and **sequential leaching**. As noted above, Galbreath and others (1999) used a float/sink density separation method with specific gravity solutions composed of mixtures of reagent-grade tetrachloroethylene and petroleum ether. After mixing and centrifugation, the float and sink samples were separated, dried in a nitrogen-purged oven and weighed. Float fractions were composed predominantly of organic (maceral-rich) with small proportions of minerals. Most minerals in the float fractions were present as tiny ( $< 5 \mu\text{m}$  in the longest dimension) inclusions within the coal particles. However, as shown in Table 2, the minerals in the float fractions still accounted for about a quarter of the total in three coals (Wyee, Eastern Canadian, and Gascoigne Wood) and nearly half in the Illinois No. 6 coal. The sink fractions were composed predominantly of larger discrete mineral grains.

Querol and others (1999) also used density fractionation. They obtained seven density fractions between  $< 1.3$  and  $> 2.8 \text{ g/cm}^3$  by using heavy liquid mixtures of bromoform, tetrachloroethylene, and xylene. It was noted that the density fractionation technique was developed for the study of high mineral matter coals. The relatively low mineral matter content of the coals in the collaborative study made complete isolation of the minerals difficult. Further, as noted above, it was also found that the mineral matter was finely dispersed in the organic matter that consequently made good density separation. It was for such reasons that chemical treatments were also used to isolate or extract mineral phases from the density fraction, specifically to extract gypsum from the  $2.0\text{-}2.4 \text{ g/cm}^3$  fraction of the Gascoigne Wood coal and to enrich pyrite by acidic attack on calcite in the  $> 2.8 \text{ g/cm}^3$  fraction of the Illinois No. 6 coal (Querol and others, 2000). Using this separation technique, Querol and others (1999) were able to assign the trace elements into the following affinity categories:

- organic matter (OM), density fraction  $< 1.3$ ;
- aluminosilicates, mainly clays (ALS);
- sulphates (GYP);
- sulphides, selenides, and arsenides (PY), density fraction  $> 2.8$ ;
- iron carbonate (CARB);
- heavy minerals (HM); and
- phosphates (PHOS).

Table 2 in Querol and others' (1999) report shows more details of the density fractions used for each coal. Querol and others (2000) later modified their density fractionation data by using a mathematical deconvolution of the chemical analyses of the whole coals and their density fractions. The mathematical deconvolution calculates the amount of organically associated elements in each density fraction. It is based on a method developed by Klika and Kolomaznik (2000) and uses the following data from the float/sink experiments:

1. mass of the coal fractions,
2. sum of crystalline phases and ash content,
3. concentrations of the trace elements in each of the coal fractions,
4. concentrations of sulphide and carbonate in each fraction.

This enables the calculation of the percentage trace element affinity to the organic part of the coal. The concentrations of the elements in the sulphide and carbonate fractions of the coal are used in a semiquantitative determination of the elemental affinities in the inorganic parts of the coal.

Huggins (1999) used a hybrid physical separation method in which the coal samples were first separated into float and tailings fractions using a Denver column flotation cell. A small fraction of the tailings product was then further subdivided by a float/sink density separation technique using bromoform with a specific gravity of 2.875. As a result of these separations, the as-received coal (RAW) was split into four fractions:

- the tailings (TAILS) from the Denver cell flotation,
- an "organic fraction" (ORG) representing the float fraction from the Denver cell,
- a "heavy minerals" fraction (HYM) representing the fraction of the Denver cell tailings that sank in bromoform, and
- a "clay" fraction (CLAY) representing the fraction of the Denver cell tailings that floated in bromoform.

The bromoform separations were not very successful. As a result, with the exception 1-2% of HYM from the Illinois No. 6 coal, the TAILS and CLAY fractions were essentially the same. The float and tailings fractions from the Denver cell were also analysed by Goodarzi and others (1999).

The other laboratories involved in the study used different sequential leaching separations. These are based on the standard method of determining the forms of sulphur in coal. Dale and Chapman (1999) used the following sequence:

1. 4.3 M hydrochloric acid (HCl) at 80°C for two hours. This dissolves oxides, carbonates, and monosulphides. The residue was then treated with
2. 0.5 M nitric acid (HNO<sub>3</sub>) at 80°C for two hours. This dissolves sulphides (pyrite). The residue was then treated with
3. 10 ml 40% hydrofluoric acid (HF) and 1 ml concentrated HCl at 60-70°C for 1 hour. 5 ml HCl and 5 ml water were then added and the mixture heated at 60-70°C for a further 1 hour. This dissolves the silicates.

The various solutions were analysed for specific trace element concentrations and the "organic" residue was also analysed. The selectivity of the pyrite leaching (stage 2) for the Illinois No. 6 coal was investigated by X-ray diffraction. It was verified that 0.5 M HNO<sub>3</sub> removed 100% of the pyrite.

Although not used in the study of the IEA collaborative programme coals, Dale and others (1999) later introduced an initial stage in which coal samples were treated with 1M ammonium acetate (CH<sub>3</sub>COONH<sub>4</sub>) at 80°C for two hours. This is similar to the first stage of the USGS sequence used by Willett and others (2000):

1. 1N ammonium acetate (CH<sub>3</sub>COONH<sub>4</sub>). This removes loosely bound ions that may be organically associated or ions absorbed on clays and dissolves some calcite. The residue was then treated with
2. 3N HCl. This removes carbonates, such as calcite, and monosulphides. The residue was then treated with
3. concentrated (48%) HF. This removes silicates, including quartz and clay minerals. The residue was then treated with
4. 2N HNO<sub>3</sub>. This primarily removes disulphides such as pyrite.

It was recognised that some silicates, such as zircon, may be resistant to the HF leaching in stage 3. The residue left includes these, other insoluble minerals, and elements "shielded" from the solvents, together with the organic portions of the coal. It should be noted that the ash yield of the residual leached coal was commonly less than 0.3 wt%, suggesting little in the way of shielded and insoluble phases in most coals.

Spears and others (1998) used the sequence:

1. shake with deionised water for up to 12 hours. This removes elements present in pore fluids and soluble minerals. The residue is shaken with
2. dilute HCl for up to 12 hours. This removes carbonates (mainly calcite), exchangeable cations and monosulphides. The residue is shaken with
3. dilute HNO<sub>3</sub> (5%) for up to 12 hours. This removes carbonates (mainly dolomite and ankerite) and some pyrite. The residue is shaken with
4. concentrated, cold HNO<sub>3</sub> and allowed to stand for up to 12 hours. This removes the remaining pyrite. The solid remaining is digested with
5. concentrated HNO<sub>3</sub> with microwave heating. This digests the organic matter. Any remaining solid is digested with
6. concentrated HCl and HF with microwave heating. This digests the silicates.

Unlike the other sequential leaching procedures, this method completely digests the coal sample leaving no "organic" residue. Some inherent problems in the technique were recognised by Spears and others (1998). For example, some of the pyrite is released in stage 3 but not quantitatively, the rest is removed in stage 4. The silicates and the organic matter will also have been partially attacked in the early stages. There is also the problem that mineral groups, such as carbonates and sulphides, do not behave uniformly.

Obviously, the data from the different groups are not strictly comparable since they were obtained from different of separation techniques ranging from simple fractionation into float and sink fractions to more complex fractionation either by density fractionation or selective leaching. Nevertheless, comparisons needed to be made, even at the risk of misinterpreting some of the data. The comparisons are published in the final overview report (Davidson, 2000) and some of them will be discussed in the presentation.

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# STANFORD-USGS SHRIMP-RG ION MICROPROBE: A NEW APPROACH TO DETERMINING THE DISTRIBUTION OF TRACE ELEMENTS IN COAL

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**Key Words:** Illite/Smectite in Coal; Ion Probe Analysis; SHRIMP-RG.

## ABSTRACT

The distribution of Cr and other trace metals of environmental interest in a range of widely used U.S. coals was investigated using the Stanford-USGS SHRIMP-RG ion microprobe. Using the oxygen ion source, concentrations of Cr (11 to 176 ppm), V (23 to 248 ppm), Mn (2 to 149 ppm), Ni (2 to 30 ppm), and 13 other elements were determined in illite/smectite, a group of clay minerals commonly present in coal. The results confirm previous indirect or semi-quantitative determinations indicating illite/smectite to be an important host of these metals. Calibration was achieved using doped aluminosilicate-glass synthetic standards and glasses prepared from USGS rock standards. Grains for analysis were identified optically, and confirmed by 1) precursory electron microprobe analysis and wavelength-dispersive compositional mapping, and 2) SHRIMP-RG major element data obtained concurrently with trace element results. Follow-up investigations will focus on the distribution of As and other elements that are more effectively ionized with the cesium primary beam currently being tested.

## INTRODUCTION

Research on the occurrence of potentially toxic trace metals in coal is fundamental to predicting the potential for distribution of these metals to the environment through coal combustion, mining, and leaching from storage piles. Microbeam instruments with good spatial resolution and element sensitivities are needed to make direct, in-situ trace-element determinations that are specific to individual coal components. The Sensitive High-Resolution Ion Microprobe with Reversed Geometry (SHRIMP-RG) at Stanford University offers these characteristics. The reversed geometry, in which the electrostatic sector is downstream of the magnetic sector of the mass spectrometer, gives the SHRIMP-RG superior mass-resolution compared to its forward geometry (FG) SHRIMP predecessor and smaller ion probes.

Our initial use of the SHRIMP-RG for coal samples focussed on the distribution of Cr and other transition metals in illite/smectite, a common inorganic clay mineral constituent of coal and other sediments. Previous work, including studies by selective leaching, electron microprobe, and XAFS spectroscopy (Huggins et al., 2000) and chemical analysis of mineral separates (Palmer and Lyons, 1996), indicates a significant residence for Cr in clay minerals in coal. This study was undertaken to confirm and quantify these results, and to demonstrate the utility of the SHRIMP-RG for studies in environmental geochemistry. Understanding the mode of occurrence of Cr in coal is especially important because the hexavalent form of the element is a known carcinogen.

## SAMPLE CHARACTERIZATION AND ANALYSIS METHODS

Samples studied include three coals currently being investigated by the USGS in Phase II of a larger DOE-funded study of toxic substances from coal combustion. The three Phase II coals are a bituminous Ohio 5/6/7 blend, a sub-bituminous Wyodak sample, and a North Dakota lignite. Three additional samples were investigated, a bituminous Illinois #6 sample from Phase I of the combustion study, a Northern Appalachian (Pittsburgh) bituminous sample and a second Illinois #6 sample studied by the USGS as part of another recent contract. Each of these samples has been very well characterized by conventional coal-testing methods, bulk geochemistry, mineralogy, and element modes of occurrence, including selective leaching, electron microprobe, and for all but the Pittsburgh and second Illinois #6 samples, bulk XAFS analysis.

Preliminary work involved characterization of illite/smectites using a JEOL 8900R electron microprobe for quantitative analysis and wavelength-dispersive elemental mapping. SHRIMP-RG data were obtained in August, 1999 and February, 2000, using an O<sub>2</sub> duoplasmatron source. Analysis points were initially subjected to a 1-3 minute burn-in to stabilize the response. The burn-in was followed by a "short" analysis consisting of 4, 7, or 8 elements, to confirm the identity of the grains selected and minimize the contribution of overlapping grains. In the August, 1999 runs, the short analyses were followed directly by "long" analyses in which the

initial 7 elements (Mg, Al, Ca, Si,  $^{52}\text{Cr}$ , K, and Fe) were re-determined and combined with analyses of Sc, Ti, V,  $^{53}\text{Cr}$ , Mn, Co, Ni, Cu, Zn, Rb, and Sr. The same procedure was used to measure these elements in reference standards. A similar procedure was followed in February, 2000, except that all the short runs were conducted successively, followed by a series of long runs for only the most promising grains. This modification minimized magnet instability caused by changes to its within-run scan range. Quantifying the concentration of Cr was the highest priority of the study, and therefore, Cr was determined twice, as  $^{52}\text{Cr}$  and as  $^{53}\text{Cr}$ . Using this approach, the natural ratio of  $^{53}\text{Cr}/^{52}\text{Cr}$  (0.1134) was typically reproduced to three decimal places. Concentrations obtained using the two chromium isotopes were generally within 1% (absolute), for calibrations obtained using the same standard (Table 1).

A variety of aluminosilicate standard glasses were investigated, including National Institute of Standards and Technology (NIST) SRM glasses 610 and 612, glass synthetic standards GSE and GSD, prepared for the USGS by Corning Glass Works, Inc., and glass prepared from powdered USGS rock standard BHVO-1. Concentrations were obtained by determining the counts/ppm for standards and calculating the concentrations of unknowns by comparing their raw counts to the standard data. Calibration results obtained using three different standards, SRM 610, GSE, and BHVO-1, for the same Ohio 5/6/7 illite/smectite, are given in Table 1. From electron microprobe analysis, the  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  contents of illite/smectite are known to be about 50 and 30 weight percent, respectively. SHRIMP-RG results for these elements are given in weight percent to facilitate comparison to the microprobe data (Table 1). For most elements, the GSE standard gives the lowest concentrations, and these can be considered minima (Table 1). GSE is the only standard determined in every SHRIMP-RG run, providing a uniform basis for comparing data from each of the runs and for all of the samples. Table 2 shows the reproducibility of counts/concentration for the GSE standard in 4 runs over a 2-day period in February, 2000. Total deviation ranges from 5.8 to 12.5%, except for Rb (20.9%) and Sr (17.9%).

Table 1. SHRIMP-RG Data Reduction and Comparison of Standards for an Ohio 5/6/7 Illite/Smectite.

August 1999	Raw Counts	Counts/ppm ( $\text{Al}_2\text{O}_3$ , $\text{SiO}_2$ in wt. %)			Concentration (ppm) ( $\text{Al}_2\text{O}_3$ , $\text{SiO}_2$ in wt. %)		
		SRM 610	GSE	BHVO	Conc. 610	Conc. GSE	Conc. BHVO
Mg	21391	9.44	13.00	13.06	2266	1645	1637
$\text{Al}_2\text{O}_3$	325487	10252	16810	17708	31.75	19.36	27.80
Ca	5442	12.68	15.57	14.59	429.2	349.5	378.0
$\text{SiO}_2$	1059325	18292	27723	19627	57.91	38.21	53.97
Sc	4163	362.6	240.5	349.6	11.48	17.31	11.91
Ti	29024	18.13	20.55	17.24	1601	1413	1683
V	13766	175.0	190.0	129.8	78.68	72.47	106.04
$^{52}\text{Cr}$	14022	180.2	215.9	163.0	77.82	64.95	86.01
$^{53}\text{Cr}$	1587	20.25	24.53	18.33	78.37	64.72	85.65
Mn	7009	200.6	303.2	253.2	34.94	23.12	27.69
Co	173	108.3	186.0	165.0	1.60	0.93	1.05
Ni	687	21.94	43.81	34.70	31.30	15.67	19.79
Rb	68370	617.4	718.8	584.2	110.74	95.12	117.02
Sr	11821	239.3	280.4	233.1	49.40	42.15	50.70

Table 2. SHRIMP-RG Results- Reproducibility of the GSE Standard.

Date	GSE standard counts per ppm (Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> in counts/wt. %)				% Total Deviation
	2 Feb 00	2 Feb 00	3 Feb 00	3 Feb 00	
Run #	1	2	3	4	
<sup>26</sup> Mg	236.5	227.5	234.0	222.7	5.8
<sup>43</sup> AlO	48462	46832	50420	47871	7.2
<sup>44</sup> Ca	44.88	43.00	46.50	44.14	7.9
<sup>44</sup> SiO	81609	79336	85934	81213	7.4
<sup>45</sup> Sc	762.3	738.3	798.6	728.8	8.7
<sup>47</sup> Ti	63.08	60.09	66.63	61.58	9.8
<sup>51</sup> V	698.0	572.0	644.1	585.8	11.0
<sup>52</sup> Cr	650.5	601.0	668.6	618.6	8.6
<sup>55</sup> Cr	72.98	68.83	75.45	69.67	8.3
<sup>55</sup> Mn	864.3	844.1	897.6	827.7	7.8
<sup>55</sup> KO	7.17	6.97	7.30	6.71	6.8
<sup>59</sup> Co	475.9	474.3	493.0	446.3	9.5
<sup>60</sup> Ni	103.8	104.1	107.07	96.12	11.0
<sup>63</sup> Cu	165.3	166.7	170.9	151.2	11.5
<sup>64</sup> Zn	84.54	87.33	88.92	76.38	12.5
<sup>72</sup> FeO	15.82	15.67	16.33	14.67	10.2
<sup>85</sup> Rb	1673.3	1673.4	1926.4	1523.8	20.9
<sup>88</sup> Sr	736.0	723.9	866.0	710.6	17.9

SHRIMP-RG RESULTS FOR ILLITE/SMECTITE

Chromium concentrations in illite/smectite in these coals range from 11 to 176 ppm (Fig. 1a). The results are consistent with semi-quantitative estimates obtained from previous electron microprobe data, leaching results, and XAFS (Huggins et al., 2000). Results for the Ohio and Pittsburgh samples are co-linear for Cr and V, possibly indicating a similar diagenetic history for these illites from the northern Appalachian Basin. Concentration ranges for some other elements of environmental interest in illite/smectite are as follows: V (23 to 248 ppm); Mn (2 to 149 ppm); and Ni (2 to 30 ppm; Fig. 1b-d). Trace element contents generally increase with the Mg content of the illite/smectite.

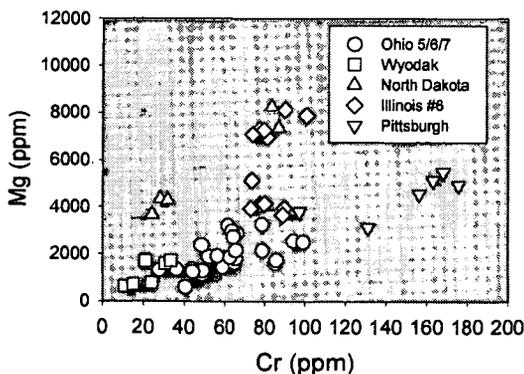


Figure 1a). Plot of Mg vs. Cr in illite/smectite from six coal samples, based on single-standard calibration using results for GSE. Illinois #6 data are for different two samples.

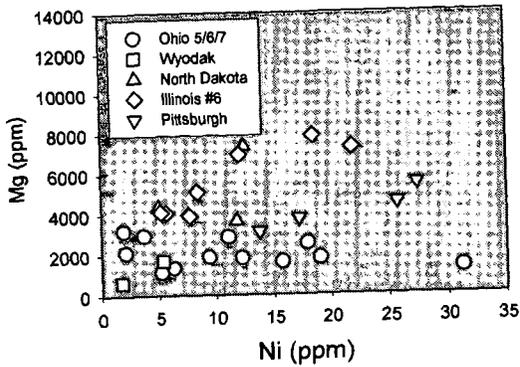
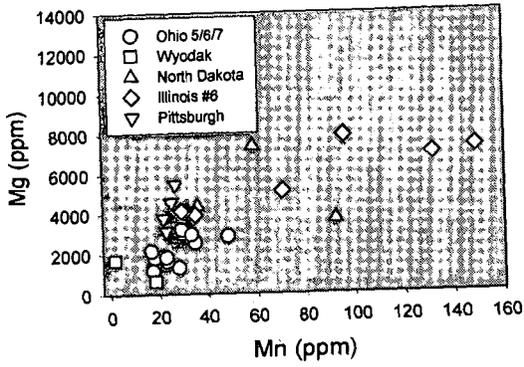
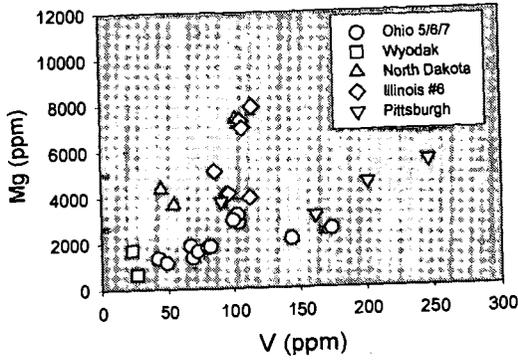


Figure 1b-d). Plots of V, Mn, and Ni vs. Mg in illite/smectite from six coal samples, based on calibration using GSE standard. Illinois #6 data are for two different samples.

## PLANNED INVESTIGATIONS

The results reported here were determined using the SHRIMP-RG in its current configuration, in which oxygen ( $O_2$ ) ions form the primary beam. Work is now being planned to take advantage of a high-energy  $Cs^+$  ion source that is expected to be available for use in the summer of 2000. In the first planned study, the distribution of arsenic in fly ash particles will be investigated with the SHRIMP-RG. This study is prompted by evidence that moderately to slightly volatile elements such as Se and As, condense on the surface of fly ash particles as they cool, contributing to the health risk from inhaled particles and the leachability of toxic elements into the environment (EPRI, 1998). Using the oxygen source, we conducted a number of preliminary tests on fly ash from a Kentucky power plant, and on the aluminosilicate glass standards. These tests showed that the  $^{75}As$  peak could be resolved from potential interferences in the GSE standard, whereas a mass scan on fly-ash in which  $^{75}As$  was present also showed a larger and broader unknown peak that is not completely resolvable from the analytical peak using oxygen ions. Count rates for arsenic are expected to be an order of magnitude higher with the cesium source.

## SUMMARY

This paper reports our initial use of the SHRIMP-RG ion microprobe for determining trace metal contents in illite/smectite, a common mineral constituent of coal and sediments. Results confirm and quantify the concentration of Cr in illite/smectite inferred from previous indirect or semi-quantitative studies. This knowledge is important in developing quantitative models for the behavior of Cr during coal processing and combustion. Planned SHRIMP-RG investigations will use a  $Cs^+$  ion beam to more effectively ionize metals such as As and Hg, thereby improving their detection and analysis.

## ACKNOWLEDGEMENT

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# DIRECT COMPARISON OF XAFS SPECTROSCOPY AND SEQUENTIAL EXTRACTION FOR ARSENIC SPECIATION IN COAL

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KEYWORDS: Arsenic, coal, sequential extraction, modes of occurrence, XAFS spectroscopy

## ABSTRACT

The speciation of arsenic in an Ohio bituminous coal and a North Dakota lignite has been examined by the complementary methods of arsenic XAFS spectroscopy and sequential extraction by aqueous solutions of ammonium acetate, HCl, HF, and HNO<sub>3</sub>. In order to facilitate a more direct comparison of the two methods, the arsenic XAFS spectra were obtained from aliquots of the coal prepared after each stage of the leaching procedure. For the aliquots, approximately linear correlations ( $r^2 > 0.98$  for the Ohio coal,  $> 0.90$  for the ND lignite) were observed between the height of the edge-step in the XAFS analysis and the concentration of arsenic measured by instrumental neutron activation analysis. Results from the leaching sequence indicate that there are two major arsenic forms present in both coals; one is removed by leaching with HCl and the other by HNO<sub>3</sub>. Whereas the XAFS spectral signatures of the arsenic leached by HCl are compatible with arsenate for both coals, the arsenic leached by HNO<sub>3</sub> is identified as arsenic associated with pyrite for the Ohio coal and as an As<sup>3+</sup> species for the North Dakota lignite. Minor arsenate forms persist in both coals after the final leaching with nitric acid. The arsenate forms extracted in HCl are believed to be oxidation products derived from the other major arsenic forms upon exposure of the pulverized coals to air.

## INTRODUCTION

The techniques of sequential leaching and XAFS spectroscopy have both been used to determine modes of occurrence of elements in coal. Both methods have their advantages and disadvantages. XAFS spectroscopy is a direct probe of the occurrence of elements and is capable of providing information on how specific elements exist in coal at concentrations as least as low as 2 ppm. The major disadvantage of the technique is that only a single spectrum is obtained which is the weighted sum of all the occurrences of the element in the coal. This problem can be largely avoided by examination of different fractions of the coal separated by various physical methods, such as float/sink in heavy liquids or froth flotation [1,2]. In addition, a database of possible occurrences of the element in coal must also be established for comparative purposes [2,3]. Finally, the method is limited to a single element at a time. Sequential leaching is an indirect method and is based upon the anticipated behavior of certain mineral types in a suite of progressively stronger acidic reagents. It has the advantage that it is a multi-element technique, although depending on the analysis methods used to determine the concentrations of the elements in the residues and solutions, the analysis time can be lengthy. As with any indirect method, sequential leaching is only as good as the assumptions on which it is based and the technique may be completely misleading if the assumptions are incorrect.

In this study, we present the first direct comparison of XAFS and sequential leaching methods for determination of elemental modes of occurrence in coal. Data from both methods are presented for the speciation of arsenic in two different coals: a bituminous coal from Ohio and a lignite from North Dakota.

## EXPERIMENTAL

### (i) Coals Investigated

Three coals were initially considered for this study: a bituminous coal from Ohio, which is a blend of coal mined from the Ohio No. 5, 6 and 7 seams, a subbituminous coal from the Wyodak seam in Wyoming, and a lignite mined from the Hagel seam in North Dakota. All three coals are used for electrical power generation at full-scale utility operations and the samplings are representative of the coal, in both composition and particle-size (~70% -200 mesh), fed to the burners at the power plants.

The trace-element contents of the two coals were determined by a combination of instrumental neutron activation analysis (INAA), inductively-coupled plasma mass spectrometry (ICP-MS), and ICP atomic emission spectroscopy (ICP-AES). Arsenic contents determined for the Ohio bituminous coal, the North Dakota lignite and the Wyodak subbituminous coal are 18, 10, and 1.7 ppm (dry basis), respectively. Owing to its very low arsenic content, the Wyodak coal was not investigated in the detail afforded to the other two coals.

(ii) Sequential Leaching Procedure

Preparation of the coal samples and the sequential extraction analysis were performed at the U.S. Geological Survey at Reston. The procedure is described in detail elsewhere [4,5]. It consists of the following sequence of extractions: (1) 1N ammonium acetate, (2) 3N HCl, (3) 48% HF, and (4) 2N HNO<sub>3</sub>. Each extraction is performed in 50 ml centrifuge tubes on a wrist-shaker, except for the extraction in HNO<sub>3</sub>, which is performed in 125 ml Erlenmeyer flasks [5]. These extractions are designed respectively to solubilize (1) exchangeable cations and some readily soluble carbonate species, (2) more resistant carbonates and simple sulfides (ZnS, PbS, CuFeS<sub>2</sub>), (3) clays and other silicates, and (4) iron disulfides (pyrite and marcasite, FeS<sub>2</sub>). After each stage, the concentrations of elements in the extract were analyzed using ICP-AES and ICP-MS and portions of the residue were saved for analysis using INAA and CVAA and also for XAFS spectroscopy.

(iii) Arsenic XAFS spectroscopy

Arsenic K-edge XAFS spectroscopy was carried out at beam-line X-18B at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, NY, during a period when the synchrotron was operated in maximum flux mode at 2.8 GeV with currents up to 400 mA. Arsenic XAFS spectra were collected in fluorescent mode using a 12-element germanium array detector [6]. The coal residue samples were suspended in the monochromatic X-ray beam by means of ultra-thin polypropylene bags. In addition to multiple scanning, both Soller slits and a 6μ Ge filter were employed to enhance the signal/noise ratio of the spectra as much as possible. XAFS spectra were typically collected at X-ray energies ranging from about 100 eV below to at least 500 eV above the arsenic K absorption edge using a rotating Si (220) double crystal monochromator to select the energy. A thin smear of As<sub>2</sub>O<sub>3</sub> on scotch tape was used as the primary calibration standard; this sample was run in an absorption experiment after the fluorescence experiment so that it provided a simultaneous calibration. The major peak in the absorption spectrum of As<sub>2</sub>O<sub>3</sub> was used to define the zero-point of energy for the arsenic XAFS spectra. It is assumed to occur at 11,867 eV.

The XAFS data collected at the synchrotron were returned to the University of Kentucky for analysis. The data were analyzed in the usual fashion [7,8]: after calibration of the energy scale, the spectra were split into separate X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) regions and each region was analyzed independently. The XANES region was used not only as a fingerprint for identification of the forms of occurrence of arsenic in the fly-ash samples, but also as the basis for extracting percentages of the different arsenic forms present in the coal sample. This was achieved by means of a calibrated least-squares analysis routine developed for analysis of arsenic XANES spectra [9], an example of which is shown in Figure 1. Owing to the low arsenic contents of the coal samples, neither the EXAFS region nor the radial structure function (RSF), which is derived from the EXAFS spectrum by mathematical manipulation [7,8], was useful for this study.

RESULTS AND DISCUSSION

(i) Sequential Leaching

Results from the sequential leaching will be reported in detail elsewhere; here, data will be presented and discussed only for arsenic. The arsenic contents of the residue fractions, determined by instrumental neutron activation analysis (INAA) after each extraction, are summarized in Table 1:

Table 1: As contents of residues remaining after leaching experiments

	Ohio bituminous As in ppm	Wyodak subbit. As in ppm	N. D. lignite As in ppm
After Amm. Acet. leach	19.1	1.7	11.0
After HCl leach	15.1	1.0	5.2
After HF leach	15.2	0.7	3.6
After HNO <sub>3</sub> leach	0.9	0.4	1.6

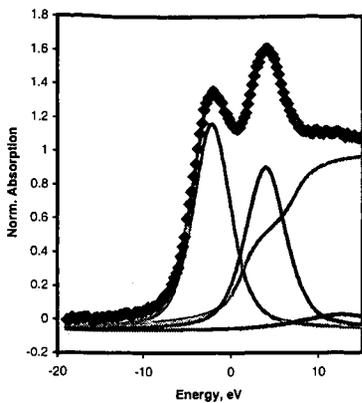


Figure 1: Least-squares fitted As XANES spectrum of Ohio bituminous coal after the ammonium acetate leach.

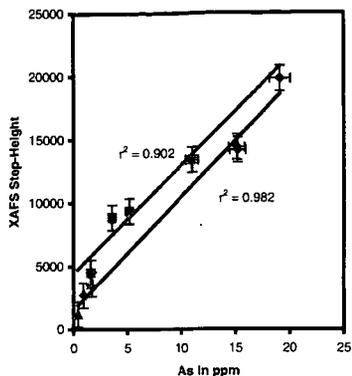
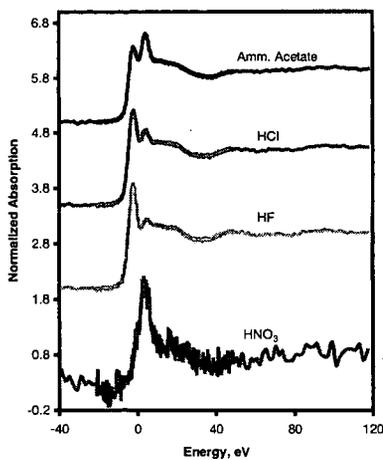
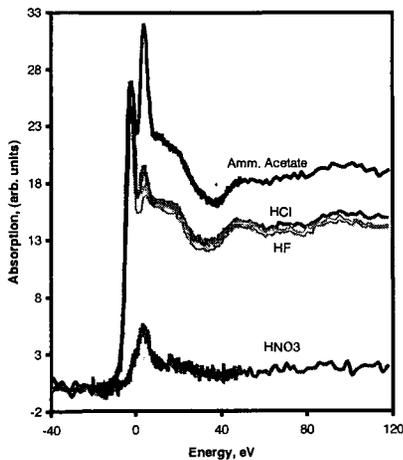


Figure 2: Correlation between the XAFS step-height and the concentration of arsenic in the leached residues.

The analytical data in Table 1 can be correlated with the step-height determined from XAFS spectra, which is also an approximate measure of the arsenic concentration. This correlation is shown in Figure 2. The correlations between the analytical data and the XAFS edge-step heights for the two coals show a reasonable approximation to a linear relationship. For the Ohio bituminous coal, the correlation coefficient ( $r^2$ ) exceeds 98%, whereas it is about 90% for the North Dakota lignite. This result indicates that both analyses are consistent with each other.

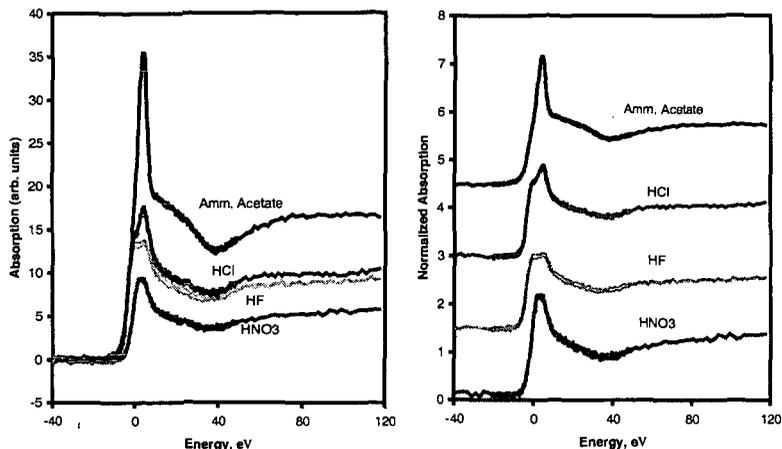


Figures 3 and 4: Unnormalized (left, Figure 3) and normalized (right, Figure 4) arsenic XANES spectra for the Ohio coal residues after different stages of the USGS leaching protocol.

(ii) XAFS Spectroscopy

Arsenic XAFS spectra were collected from the various fractions using as many as 10 scans for each sample. The spectra are shown in Figures 3 and 4 for the Ohio bituminous coal and in Figures 5 and 6 for the North Dakota lignite. Figures 3 and 5 show the unnormalized spectra, whereas Figures 4 and 6 show the same spectra normalized to the edge step and hence, these latter groupings of spectra have the effect of concentration removed from them. The data clearly show, by the reduction in intensity of the major peak at about 4.0 eV, that the HCl treatment removes principally, if not exclusively, arsenate from both the Ohio and North Dakota coals. This observation confirms more definitively the similar conclusion made in Phase 1 of this study

[4,10] based on a less direct comparison of leaching data and arsenic XAFS data for various coals. The data show also that the HF treatment has little effect, except for removing some very minor amounts of arsenate remaining after the HCl treatment. For the Ohio coal, as indicated by the reduction in intensity of the peak at about  $-2$  eV, the  $\text{HNO}_3$  treatment removes all of the pyritic arsenic. However, no such phase is present in the North Dakota lignite. Rather for this coal, the  $\text{HNO}_3$  treatment appears to be removing an  $\text{As}^{3+}$  phase, as the peak that is removed is close to 0 eV. For both coals, there is a small residue of arsenic that remains after all the leachings. It is not arsenical pyrite or  $\text{As}^{3+}$ , but rather more like an arsenate phase.



Figures 5 and 6: Unnormalized (left, Figure 5) and normalized (right, Figure 6) arsenic XANES spectra for North Dakota Lignite residues after different stages of the USGS leaching protocol.

A calibrated least-squares fitting model, developed earlier for quantifying arsenic species in bituminous coals [9], was used to quantify the arsenic speciation in the Ohio bituminous coal samples. For this coal, it was decided to fit only the two major arsenic forms present: arsenical pyrite and arsenate. Using this procedure [9], the arsenic speciation results obtained for the Ohio bituminous coal are summarized in Table 2. The least-squares fitting model has not yet been modified for application to the low-rank coals and their different arsenic species.

Table 2: Estimates of arsenic forms remaining after each leaching step in the Ohio coal

Leachant	%As as As/pyrite	%As as Arsenate	ppm As as As/pyrite	ppm As as Arsenate
Amm. Acetate	75	25	14.3	4.8
19.1 ppm As remains				
HCl	93	7	14.0	1.1
15.1 ppm As remains				
HF	>95	<5	>14.4	<0.8
15.2 ppm As remains				
$\text{HNO}_3$	<10	>90	<0.1	>0.8
0.9 ppm As remains				

Based on this analysis, the concentration of arsenic as As/pyrite after the first three leaching steps is approximately the same,  $14 \pm 1$  ppm. This indicates that none of the three reagents, ammonium acetate, HCl, or HF removes significant arsenic as As/pyrite. As has been postulated previously [9], the presence of arsenic in pyrite appears to make pyrite more reactive to oxidation. However, for this particular coal, it does not appear that any arsenic associated with pyrite is leached prior to the  $\text{HNO}_3$  treatment. The HF leach appears to remove only the minor arsenate remaining after the HCl leach. The  $\text{HNO}_3$  leach removes all of the arsenic as arsenical pyrite and appears to leave a small residue of arsenate on the carbonaceous materials. It should be noted that the arsenate in the  $\text{HNO}_3$  residue is higher than that remaining after the HF leach, suggesting that it has been formed during the nitric acid leach.

XAFS examination of different aliquots of the two coals about a year apart shows a significant enhancement of arsenate in both coals during this time period. The arsenate species is clearly an oxidation product of other arsenic forms in the coals. Furthermore, even though the coals are not

deliberately oxidized, such oxidation is an on-going process once the coal is crushed and exposed to air. Hence, the leaching results are likely to be found to change systematically with time, reflecting this time-dependent change in arsenic speciation.

## CONCLUSIONS

The use of arsenic XAFS spectroscopy to examine arsenic in leached residues of coals from a sequential leaching protocol for elemental speciation in coals has provided unparalleled insight into the leaching characteristics of arsenic from coal and enables a rather complete assessment of the assumptions behind using sequential leaching for arsenic speciation to be made. XAFS spectroscopy shows clearly that the major fraction of arsenic leached from both coals by HCl is arsenate and that HNO<sub>3</sub> removes much of the remaining arsenic in both coals. Leaching with HF has little effect on the arsenic content of both coals examined and appears restricted to removing any arsenate species that remains after the HCl leach. The arsenic associated with pyrite in the bituminous coal is removed effectively by nitric acid, but a quite different form is removed from the lignite by nitric acid. The XAFS data suggest that this arsenic phase may be an As<sup>3+</sup> species, but it remains yet to be positively identified. Finally, a small fraction of the arsenic (5-15%) remains in the coal after the nitric acid leach. We suspect that this is an organoarsenate formed by a side reaction between the arsenic leached from the coal and new oxygen functionality on the coal introduced by reaction of the coal macerals with nitric acid.

## ACKNOWLEDGEMENTS

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## ROUND ROBIN ON BIOMASS FUELS

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Keywords: Biomass analysis, digestion, analysis methods

### INTRODUCTION

In order to optimise the use of biomass as a fuel it is essential to have reliable information about its chemical composition. Therefore, it is of great significance to have useful methods for detecting the complete composition of the fuel. By means of Round Robins the commonly used methods can be evaluated and rated.

### OBJECTIVES

The data gained from the Round Robin shall provide a representative overview of the common methods for biomass characterisation used in the laboratories. It will give detailed information about all analysing steps (sample preparation, digestion methods, and analysis). The evaluation will cover in first place the interlaboratory scattering of results. Laboratories using similar methods of analysis will be gathered and evaluated separately. Due to the fact that no reference samples for biomass are available it will not be possible to assess the accuracy of the analytical data.

### IMPLEMENTATION

Two fuel samples of wood and straw were investigated in the Round Robin. The fuels were milled and homogenised by an independent laboratory and then checked for homogeneity by analysing for some major elements (C,N,S,K,Fe). In the Round Robin the probes were analysed for 35 parameters by 39 German and European laboratories. All participating laboratories were free to choose the analytical methods they are used to, only recommendations concerning available experience and possible problems that might occur were supplied. Moreover, the laboratories were free to use several different methods in parallel to compare the obtained results. In order to be able to compare the different methods, the laboratories should fill in a detailed questionnaire to clearly describe each step of preparation, digestion, and analysis itself. Based on this information a comparison of the influence of each single analysis step was possible.

### EVALUATION

The classical evaluation of a Round Robin is based on ISO 5725. The assumption for using this standard is the Gaussian distribution of the data. A normal distribution is based on random mistakes scattering around the accurate value. In a Round Robin where each laboratory was recommended to use its own well proven analytical methods the interlaboratory mistakes will be systematic [1]. In this Round Robin the gained data is very inhomogeneous and therefore, a few data may have a big influence on the location parameters.

Consequently, a distribution free, robust method based on Hampel was used for statistical evaluation. This method does without elimination of so called outliers, which are weighted instead making the results less sensitive to extreme single values [2].

In order to illustrate the statistical calculations the results are shown in evaluation diagrams. Some of the terms mentioned can be defined as follows:

"Wiederholstandardabweichung",  $V_r$ , corresponds to the mean value of all intralaboratory standard deviation  $S_r$ , divided by the "robust" mean value.

"Vergleichstandardabweichung",  $V_R$ , corresponds to the mean value of the interlaboratory standard deviation  $S_R$ , divided by the "robust" mean value.

The values measured by the laboratories are represented in the diagrams by bars. The centreline of each bar shows the robust mean value, the standard deviation corresponds to the distance between the centreline and the outside bounds of the bar.

### RESULTS

As an example for using biomass as a fuel the analysis results for chlorine and ash content that are important for the combustion and slagging/fouling behaviour in furnaces are presented.

KCl in the fuel could be released as KCl or converted into HCl, Potassium silicate and  $K_2SO_4$ . At combustion temperature KCl is released into the gas phase and condenses at the heat surfaces at lower temperatures. Condensed KCl on tube surfaces could form low melting eutectics, leading to an increased corrosion rate [4].

The ash content affects the ashing device and the ash disposal as well as the concept and the cleaning of the heat exchanger.

Figure 1 shows the evaluated chlorine contents of the straw sample. The robust mean value of all laboratories is 1263 mg/kg (db), the range between the single mean values ranges from 745 mg/kg (db) up to 2391 mg/kg (db).

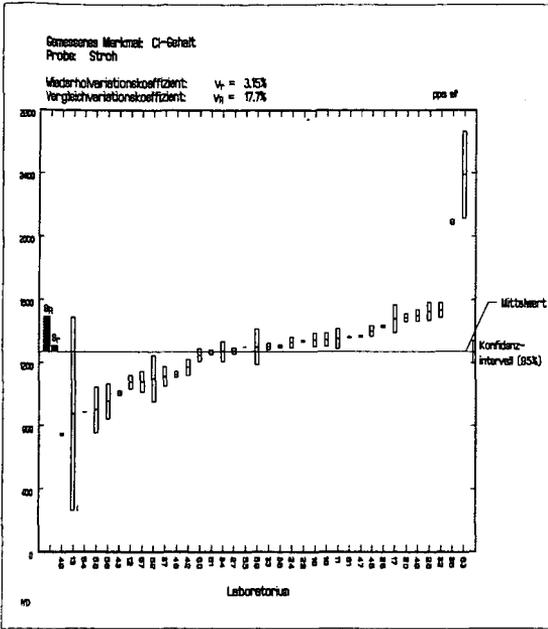


Figure 1: Chlorine in straw

In order to evaluate some single laboratory values the sample preparation, digestion and measurement procedures are shown in Table 1 and 2. Some of the results can be explained as follows:

- Preashing the sample will lead to a loss of volatile matters (Lab 49)
- Using Eschka-mixture (Labs 12, 37) is also not recommended for Cl detection, because volatiles will be lost when putting the probe for 1h in an 675°C heated muffle furnace. This was also reported by [3].

- The low temperature and low pressure of the "Wurzschmitt"-Digestion (Lab 58) may lead to bad results
- Due to a single analysis the results from Lab 54 are not considered.

In order to go one step further, the laboratories were divided into several groups of similar digestion methods. This shows whether the analysis results will be more comparable for laboratories using comparable digestion methods. **This is no classification or benchmarking of the laboratories.**

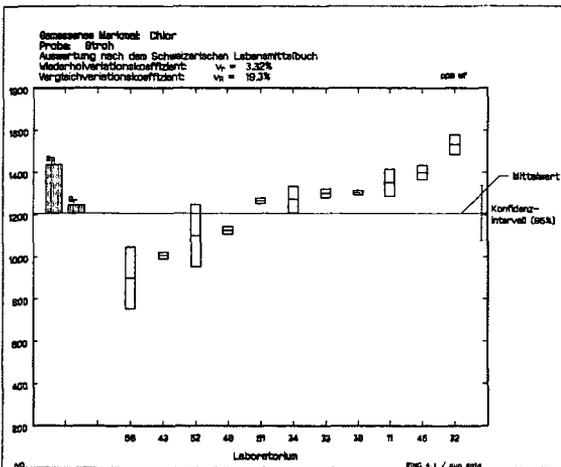


Figure 2: Chlorine in straw analysed by reduced methods

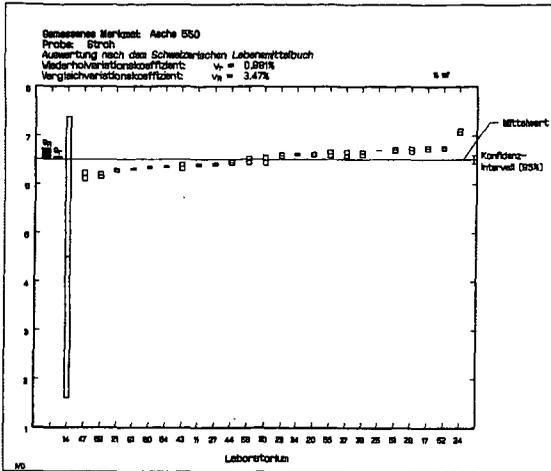


Figure 3: Ashcontent of straw at 550°C

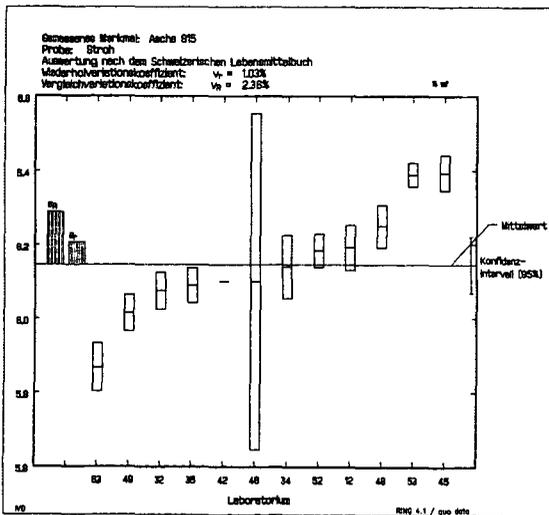


Figure 4: Ashcontent of straw at 815°C

## DISCUSSION AND CONCLUSIONS

One of the major problems when analysing biomass is the non-homogeneity of the fuel and therefore, the collection of a representative probe. The reason for "outliers" is often the small sample-mass taken for the digestion.

Comparing the results from different laboratories using suitable methods for analysing chlorine in the fuel it can be seen that the values scatter in a range of  $\pm 25\%$  around the robust mean value although they were using very different methods. Even digesting the sample by eluting it with water shows very good results. This confirms the assumption that chlorine in Biomass is mostly inorganically bound, whereas the organically bound part is very small. The elution method facilitates to use larger sample quantities for the digestion, with which a better homogeneity can be reached. Reducing the possible digestion methods does not lead to a better comparability of the results. This underlines the previously mentioned problem of the non-homogeneity of the fuel. The ash content of the fuel is strongly connected to the ashing temperature since at higher temperatures more volatile matters are released. The amount of volatiles in biomass (>75%) is very high compared to coal ( $\approx 35\%$ ). It is recommended that ash content should be determined at 550°C, because the volatile elements in a combustion plant condense in the fly ash and therefore must be considered in the ash balance.

Figure 2 shows laboratories using a combustion method collecting the combustion products in an alkali solution.

This makes it clear that reducing the analysis methods for chlorine detection does not lead to more comparable results.

Due to the free choice of analytical methods the ash content was determined in a temperature range of 550°C up

to 900°C. Figure 3 and 4 show the measured results.

The high standard deviation of Laboratory 14 in figure 3 can not be explained. The results from other labs scatter in a range of  $\pm 7\%$  around the robust median value of 6,5% (db). The methods used are all based on the principle of ashing the probes till constant weight. They only differ in sample preparation (milled, unmilled, preashed, or humidified). The ash content determined at 815°C shown in Figure 4 has a mean value of 6,18% (db), which is significantly lower than the 550°C values.

## ACKNOWLEDGEMENTS

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Table 1: Analysis Methods

Lab	Preparation	Amount	Digestion	Method	Lab	Preparation	Amount	Digestion	Method
		[mg]					[mg]		
11	1000	1100	03b	12	43	1005	300	03b	19
12	1000	1100	05	12	45	1000	20	02e	20
13	1000	200	02d	06	46	1000	20	02d	20
17	2300		03c	12	47	1000	1000	14	06
20	1000	5000	12c	06	48	1000	250	07	06
22	1000	500	20	12	49	1000	500	04	12
24	1000	10000	13	06	51	1000	700-800	03a	06
25	1303	5500	21	14	52	1000	100-200	17	06
27	1000		20	06	54	1002	1000	03c	06
29	1004		21	14	56	1000	400-600	03a	12
32	1000	400	03a	06	57	1000	1000-2000	07	12
33	2302	2-10	02e	12	58	1000	100	16	06
34	1001	15000	03b	06	59	1000	220	03c	06
35	1003	200	03a	06	60	1001	220	03c	06
36	1000	800	02	06	61	1001	1000	14	06
37	2300	1100	05	12	63	1000	130	03a	06
42	1000	2000	04	06					

Table 2: Method-Code

Digestion		Analysis					
2	Combustion in Oxygen	6	IC				
3	Calorimetric Bomb	12	Titration AgNO <sub>3</sub>				
4	Wickbold	14	XRF				
5	Eschka	19	Ion Sensitive Electrode, ISE				
7	Eluting with HNO <sub>3</sub>	20	Mikrocoulorimeter				
12	Ashing						
13	Aqueous Solution (hot) 10g/250 ml		<b>Chemicals</b>				
14	Aqueous Solution (hot) 5g/250 ml	a	Alkali Solution and H <sub>2</sub> O <sub>2</sub>				
16	Wurzschmitt	b	Alkali Solution				
17	Grote-Kreker	c	In Water				
18	Melting Digestion	d	In Aqueous H <sub>2</sub> O <sub>2</sub> -Solution				
20	Aqueous Solution	e	In Acid and Acetate - Solution				
21	Pellet						
<b>Sample Preparation</b>							
1	As recieved	0	20°	0	Air	0	No extra milling
2	dried	3	105°	1	N <sub>2</sub>	1-5	Extra milling

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# USE OF CHEMICAL FRACTIONATION TO PREDICT BIOMASS FUEL ASH BEHAVIOUR

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**KEYWORDS:** biomass, ash deposition, selective extraction

## ABSTRACT

Chemical Fractionation (CF) has been proposed by several researchers as a tool to assist in the advance prediction of biomass fuel ash behaviour. In this work, the relation between CF classes and alleged behaviour during pf combustion is studied experimentally. Samples of well-analysed fuel batches - wood, straw and chicken manure - have been subjected to a scheme of selective extractions. After each extraction, a subsample of the partly extracted material was used as a fuel in a lab-scale combustion and ash deposition test. Comparison of the ash deposits obtained with original and selectively extracted fuels yielded valuable information on the practical use of selective extraction for the prediction of biomass fuel ash behaviour. Suggestions for improvement of the extraction scheme are also given.

## INTRODUCTION

Chemical Fractionation (CF) is a method to discriminate inorganic classes in biomass fuels according to their solubility in a sequence of increasingly aggressive solvents [Baxter, 1996]. The parts of the fuel found as either water soluble, ion exchangeable, hydrochloric acid soluble or residual (non-soluble) are subsequently related to their alleged behaviour in a process like e.g. pulverised fuel combustion. Generally, the water soluble and ion exchangeable classes include various salts of potassium and sodium which are considered to be easily vaporised in a high temperature process. Carbonates and sulphates are expected in the hydrochloric acid soluble class [Baxter, 1996], while the oxides, silicates and sulphides are not extracted and classified as residual. Both the hydrochloric acid soluble and residual matter are considered to be much less reactive in a thermal process.

The proportion of the elements of interest found in the first two classes is mostly interpreted as a measure for the release of reactive inorganic species to the gas phase. Their availability is subsequently related to enhanced deposition of ash on boiler and heat exchanging surfaces.

So far, ash deposition has been studied using fuels as a whole. In the current study, selective extraction has been applied to produce fuels lacking specific inorganic species. These fuels have been used in lab-scale deposition tests to verify the alleged relations with the currently used CF classes.

## EXPERIMENTAL

Wood, straw and chicken manure with well-known inorganic compositions (threefold ICP-AES analysis per fuel) have been tested with respect to their ash deposition behaviour in a lab-scale combustion simulator. In Figure 1, a schematic view of the installation is given. By means of a staged gas burner and electrical furnace, the gas temperature and gas phase concentrations of O<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, SO<sub>2</sub> and N<sub>2</sub> have been set to simulate typical combustion conditions in a pulverised fuel boiler. Fouling of superheaters was simulated by means of a temperature-controlled metal deposition surface, with a surface temperature of 600 °C at a gas temperature of 1200 °C. The surface temperature was recorded during the deposition test. The deposits were analysed off-line in 2D and 3D by means of SEM-EDX. The results serve as a reference for comparison with the deposition behaviour of partly extracted fuels.

The same fuels were subjected to a sequence of three selective extractions using water, a 1 M NH<sub>4</sub>Ac solution and a 1M HCl solution. The procedure suggested by Baxter [1996], see Figure 2, was evaluated by a) comparing the composition of the extracted material with the extract concentrations, b) comparing parallel to sequential extraction, c) examining the effect of pH-control during the extraction and d) evaluating multiple extractions at a low L/S ratio versus a single extraction at a proportionally higher L/S ratio. From these tests, suggestions for improvement of the procedure are given. Extracted material has been taken from each extraction step to be used as a fuel in a deposition test in the facility described above. Again, SEM-EDX was used to examine the deposits and to compare the occurrence of specific species in these deposits with those obtained from burning the original fuels.

## RESULTS

Extraction at a L/S ratio of 3 is not feasible for biomass such as wood or straw due to a very high water uptake. An L/S ratio of 10 or more should be used in stead.

The determination of extracted elements is much easier and cheaper by analysing the extract than by handling and opening up and analysing the extracted solid residue.

The pH-value after equilibration of the solvent with the solid phase is influenced by and depends on the biomass used. Control of the pH-value at a pre-set constant value may be considered but care must be taken not to replace a pH-influence on the extraction process by an influence of increased ion concentrations in the solvent.

Partly extracted fuels have been used in lab-scale ash deposition tests under simulated pf firing conditions. The deposits are compared to those obtained from the original fuels by means of 2D and 3D SEM-EDX analysis, identifying the presence and role of relevant species in the deposit. Heat fluxes through the growing deposit layers have been determined as a function of time as a more quantitative measure of deposit development. Definite results will be presented by the time of the symposium.

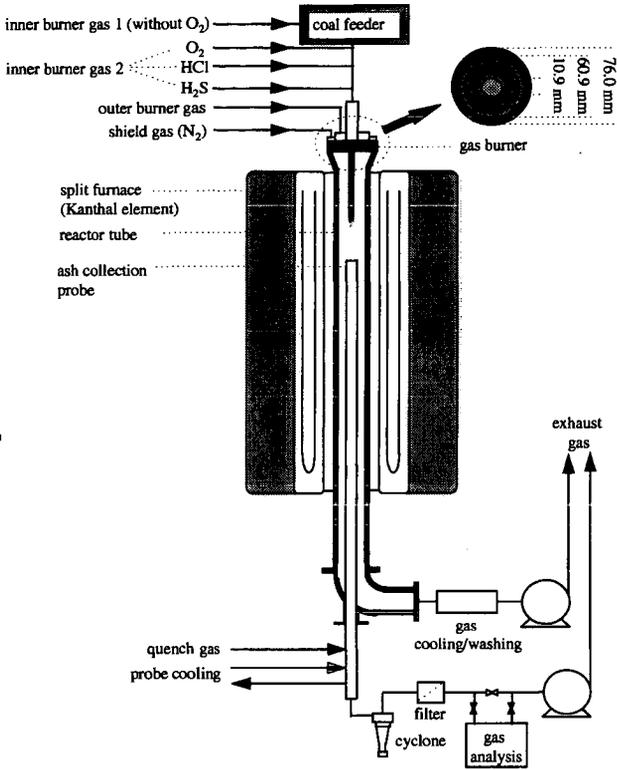
## DISCUSSION AND CONCLUSIONS

- Selective extraction schemes which are currently used for predicting fuel ash behaviour have been designed - in the past - for the evaluation of leaching characteristics of soils. For a Chemical Fractionation analysis of biomassfuel inorganic matter, an adapted design should be aimed at the selective extraction of elements of interest applying specific pH-values and/or solvent ion concentrations. It may be necessary to control these conditions to eliminate effects of the fuel (biomass) matrix during the extraction. More work is needed to establish specific conditions for extracting key elements or species with a known behaviour in thermal processes.
- Up till now, only a gross difference between water soluble / ion exchangeable, strong acid soluble and non soluble inorganic species can be made using three selective extractions. A definite relation between extraction results and fuel ash behaviour can be obtained using fuels which have been partly extracted under well-controlled conditions in subsequent combustion tests aimed at ash deposition evaluation. From this, extraction schemes can be set up for the determination of specific, predefined inorganic species.

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FIGURES



Typical particle feed rate (g/h)	1
Particle residence time (ms)	10 – 3000
Particle heating rate (°C/s)	> 10 <sup>5</sup>
Gas supply inner burner	CH <sub>4</sub> , CO, CO <sub>2</sub> , H <sub>2</sub> , N <sub>2</sub> , O <sub>2</sub> , H <sub>2</sub> S
Gas supply outer burner	CH <sub>4</sub> , CO, H <sub>2</sub> , O <sub>2</sub> , H <sub>2</sub> S
Operating pressure (MPa)	0.1
Reactor tube inner diameter (m)	0.076
Reactor tube length (m)	1.0
Max. electrical heating temperature (°C)	1600
Probes for:	gas temperature/ composition measurement; ash & deposit collection

Figure 1. Schematic overview of the Atmospheric Entrained-Flow Gasification and Combustion simulator, and its main features.

**Chemical fractionation procedure  
according to L.L. Baxter**

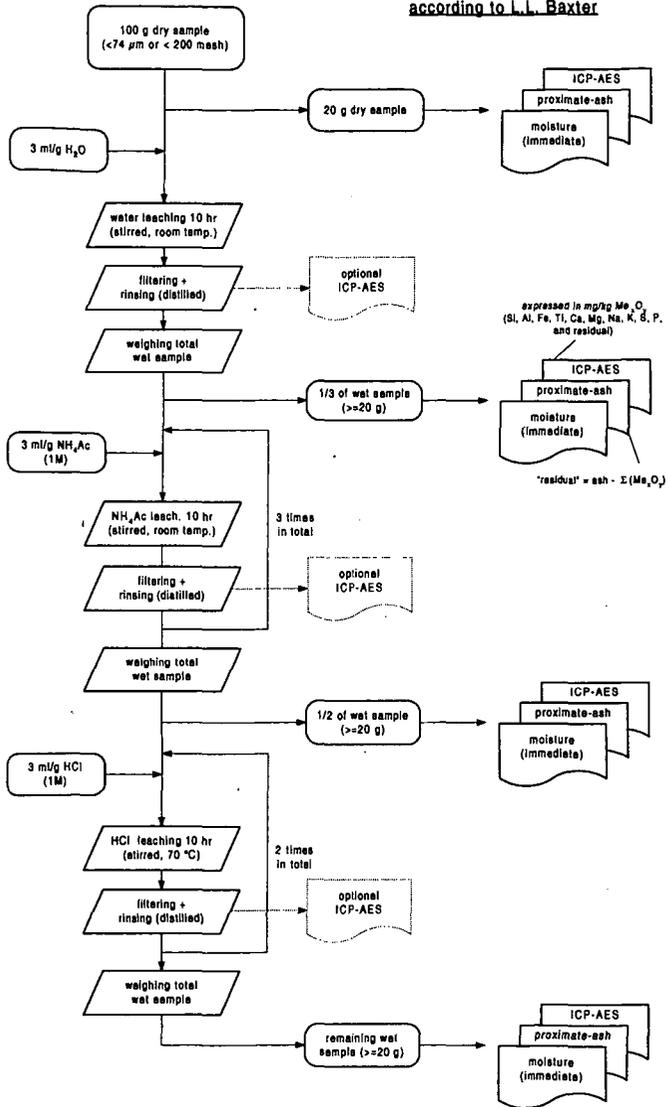


Figure 2. Extraction scheme used for Chemical Fractionation analysis of inorganic matter in biomass fuels (Baxter, 1996).