

Extraction of Trace Elements in Coal Fly Ash and Subsequent Speciation by High-performance Liquid Chromatography with Inductively Coupled Plasma Mass Spectrometry*

Plenary Lecture

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The speciation of arsenic in coal fly ash is reported. The amounts of As^{III} and As^{V} were found and these values, released into water from coal fly ash, are dependent on the pH of extracted solution and the type of coal fly ash (*e.g.*, location collected, type of coal and combustion conditions). A small amount of arsenic conversion from As^{III} to As^{V} was found, especially from the lower pH extractions. The arsenic conversion may be caused by co-existing high oxidation states elements in the extracted solution, and may be promoted by the grinding process. Oxygen from the atmosphere was found to be an unlikely source for the arsenic conversion. A preliminary investigation for speciation of vanadium and nickel in coal fly ash shows that V^{V} , V^{IV} and Ni^{II} exist in the extracted solutions. This extraction-speciation approach can provide some basic information for predicting the hydrolytic behaviour of trace elements in the coal fly ash-water systems and can be extended to the speciation of other elements.

Keywords: *Inductively coupled plasma mass spectrometry; high-performance liquid chromatography; speciation; arsenic; vanadium; nickel*

The total amount of potentially hazardous toxic elements in coal fly ash is relatively small, however there may be significant contributions to the environment since a large amount of coal fly deposits on the land surface every year. There is an increasing interest in trace element speciation of coal fly ash due to the toxic nature of many of its components and because the toxicological profiles of some of the potentially hazardous compounds depend on their total amount, and on the oxidation states or chemical forms of the elements. For example, several arsenic compounds such as arsenite (As^{III}), dimethylarsinate (DMA), monomethylarsonate (MMA) and arsenate (As^{V}) have various toxicities. Among them, As^{III} is the most toxic form, about 50 times more toxic than As^{V} and several hundred times more toxic than MMA or DMA.^{1,2} Chromium(III) is an essential element for the maintenance of glucose, lipid and protein metabolism. However, Cr^{VI} is known to be toxic because of its ability to oxidize other species. Exposure to chromium(VI) can result in various forms of cancer.^{3,4} Vanadium(V) has also been determined to be more toxic than vanadium(IV).⁵ Standard reference materials (SRM) (*e.g.*, Coal Fly Ash 1633a, 2689, 2690 and 2691) from the National

Institute of Standard and Technology (NIST) have only the total amount for each trace element provided.

The speciation of arsenic in various samples has been performed by high-performance liquid chromatography (HPLC) coupled with inductively coupled plasma mass spectrometry (ICP-MS)⁶⁻¹² or with inductively coupled plasma atomic emission spectrometry (ICP-AES).¹³⁻¹⁸ The speciation of chromium with ICP-AES^{4,15,19} and the speciation of vanadium with ICP-MS detection^{20,21} has also been reported.

A difficulty with speciation lies in the successful removal of these trace elements from coal fly ash solid, without changing their oxidation states or chemical forms. Most digestion procedures involve harsh conditions, which may change any of the original forms of the element to only one of its species. In this study, the procedures for trace element speciation in coal fly ash solid samples have been performed in the following order: (a) extraction of coal fly ash with water at various pHs (pH=1-12, extraction may occasionally be referred to as dissolution); (b) determination of trace elements in solutions of various pH values with ICP-MS; and (c) speciation of trace elements in the extracted solution from coal fly ash solid by HPLC-ICP-MS. The ICP-MS detection is chosen for its ultra-trace level detection capabilities. The extraction strategy is to study the effect on total trace element and individual trace element species by varying pHs, grinding and/or sonicating. Because of the relatively mild extraction conditions, total amounts of the various elements in the fly ash are not extracted. However, these extraction conditions are more representative of the actual environmental risk than the conditions imposed by harsh total digestion methods. A detailed study of arsenic speciation and a preliminary investigation of the speciation of vanadium and nickel are also reported.

EXPERIMENTAL

Instrumentation

A commercial ICP-MS instrument (VG PlasmaQuad II STE, VG Elemental, Winsford, Cheshire, UK) was used for all data acquisition. The operating conditions are shown in Table 1. A concentric nebulizer (C-Type, Precision Glassblowing, Colorado, Englewood, CO, USA) and a double-pass Scott-type spray chamber (Precision Glassblowing) cooled to 5 °C by means of a refrigerated chiller (Neslab Instrument, Portsmouth, NH, USA) were used. The spray chamber was maintained at 5 °C to reduce the amount of solvent vapour (thereby reducing condensation in the torch elbow) reduce oxide interference, and improve plasma stability.

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Table 1 ICP-MS operating conditions

ICP system	
Forward power/W	1350
Reflected power/W	<2
Coolant flow rate/l min ⁻¹	12
Auxiliary flow rate/l min ⁻¹	1.5
Nebulizer flow rate/ml min ⁻¹	750
Sampling depth*/mm	12
Mass spectrometer	
Sampler (nickel) orifice/mm	1.0
Skimmer (nickel) orifice/mm	1.0
1st stage pressure/mbar	1.9
2nd stage pressure/mbar	<1 × 10 ⁻⁴
3rd stage pressure/mbar	<2 × 10 ⁻⁶
Dwell time/ms	320
Channels/u	20
Sweep time/s	0.5
Mass range (m/z)	6–239
Scanning time/s	60

* Defined as the distance between the front coil of the load coil and the tip of the sampling cone.

A Dionex Model DX-300 HPLC System (Dionex, Sunnyvale, CA, USA) and a Rheodyne Model 9125 injector (Cotati, CA, USA) were used. Samples were injected using a 100 µl loop. A Wescan Anion/R IC column (250 mm × 4.1 mm id, Wescan Instrument, Deerfield, IL, USA) was used for the speciation of arsenic. A 45 cm length Teflon PTFE tubing (0.012 in id and 0.030 in od, Cole-Parmer, Niles, IL, USA) was used to connect the column to the concentric nebulizer. The eluent 1 (2% propanol) used in the speciation of arsenic was prepared from propan-1-ol (HPLC grade, Fisher Scientific, Fair Lawn, NJ, USA) with distilled de-ionized water (18 MΩ, Barnstead, Newton, MA, USA). Eluent 2 (50 mmol l⁻¹ carbonate buffer) was prepared from ammonium carbonate and ammonium hydrogen carbonate (Fisher Scientific) and distilled de-ionized water (adjusted to pH 7.5 by ammonia solution). A gradient programme was used for the speciation of arsenic. At the beginning, 70% of eluent 1 (2% propan-1-ol) and 30% of eluent 2 (50 mmol dm⁻³ carbonate buffer) were run for 3 min. The mobile phase was then stepped to 100% eluent 2 until the separation was completed.⁵ The flow rate was kept constant at 1 ml min⁻¹.

A mixed mode column (250 mm × 4 mm id, HPLC-CS5, Dionex, Sunnyvale, CA, USA) was used for the speciation of vanadium and nickel. The eluent was prepared by dissolving lithium hydroxide followed by the addition of 2,6-pyridine dicarboxylic acid. The pH of the mobile phases were adjusted to 3.6 using concentrated nitric acid for the speciation of vanadium and to 6.8 using ammonium hydroxide for the speciation of nickel as specified by Tomlinson *et al.*²⁰

Reagents and standards

Nitric acid solution (2% m/m) was prepared from doubly distilled concentrated nitric acid (GFS Chemicals, Columbus, OH, USA) with distilled, deionized water. Multi-element stock solutions (10 mg g⁻¹) of V, As, Zn, Ni, Mn, Cr, Pb and Cd were prepared from 1000 mg ml⁻¹ single element stock solutions (Certified Atomic Absorption Standards, Fisher Scientific) in 5% nitric acid and 5% hydrochloric acid, respectively. Multi-element standard solutions for the external standard calibration were prepared by serial dilution of the multi-element stock solutions with 2% nitric acid. Two sets of standard solutions, 5, 20, 50 and 100 ng g⁻¹ as well as 10, 100, 500 and 1000 ng g⁻¹, were used to construct calibration graphs for the analysis of extracted solutions containing low and high levels of analytes.

Stock standard solutions of As^{III}, As^V, DMA and MMA

were made from NaAsO₂ (As^{III}), Na₂HAsO₄·7H₂O (As^V), (CH₃)₂AsO·OH (DMA) and CH₃AsO₃Na₂·6H₂O (MMA) (Sigma, St. Louis, MO, USA). Standard solutions ranging from 2 to 100 ng g⁻¹ were injected into the HPLC-ICP-MS system for preparing the calibration curve.

Stock standard solutions were made using vanadyl(IV) sulfate trihydrate [VOSO₄·3H₂O] for V^{IV}, ammonium metavanadate (NH₄VO₃) for V^V and nickel(II) nitrate hexahydrate [Ni(NO₃)₂·6H₂O] for Ni^{II}. All were purchased from Aldrich Chemical Company (Milwaukee, WI, USA).

Extraction From Coal Fly Ash

Effect of varying pH

Coal Fly Ash SRM 1633a (NIST, Gaithersburg, MD, USA) was weighed (1 ± 0.001 g) in an HDPE bottle (Nalge, Rochester, NY, USA) using an electronic balance (Sartorius, Bonemia, NY, USA). Then 20 g (±0.001 g) of distilled de-ionized water (DDW, pH 7) or water at various known pH values were carefully introduced into the bottle. Magnetic stirring bars (1/2 in long × 1/8 in od, Fisher Scientific) and a Thermix stirring hot-plate (Model 610T, Fisher Scientific) were utilized to stir the suspensions continuously at room temperature (18 °C) for 7 d. The extractants with known pHs (water at various pHs) were prepared by diluting stock solutions of HNO₃, H₂SO₄ and HCl with distilled de-ionized water, in order to study the effects of different pHs and different types of acid. Concentrations of HNO₃ and H₂SO₄ were at low levels; even the solution at pH=1 required only a few drops of stock acid solution. It is assumed that no oxidation–reduction reaction takes place due to HNO₃ and H₂SO₄ during the process of extraction. The extractants made from diluted HCl solution were used to study the possible polyatomic interferences formed in the ICP on the determination of analytes, such as ⁴⁰Ar³⁵Cl⁺ on ⁷⁵As⁺, and ³⁵Cl¹⁶O⁺ on ⁵¹V⁺. The extractants prepared from NaOH and Na₂CO₃ (certified ACS, Fisher Scientific) were to study the effect on the trace element solubility due to different bases. The pH values of extracted solutions were measured by a pH meter (pHTestr 2, Cole-Parmer). No significant changes in pH were observed before and after the neutral water extraction of SRM 1633a.

Effect of grinding and ultra-sonication

A planetary micro grinding mill (Fritsch GmbH, Idar-Oberstein, Germany) was used to obtain a small particle size of coal fly ash. The procedure is the following: an appropriate amount of Coal Fly Ash SRM 1633a was placed in a grinding bowl equipped with grinding balls (Syalon, containing 90% silicon nitride). After carefully inserting the bowl into the recess of the bowl plate, the grinding mill was turned on and operated continuously for 24 h. No apparent heating was observed during the grinding process, nor contamination from the grinding bowl and balls, determined by analysis of the solution washed out from the grinding bowl and balls after 3 h grinding with no coal fly ash present. The final particle size of the ground coal fly ash was estimated to be from 3 to 10 µm according to the manufacturer's information. The ground coal fly ash in a pH 7 solution was sonicated for 5 h using an ultra-sonic bath (Fisher Scientific) and then the suspension was extracted for 7 d.

Effect of extraction time and temperature

Coal fly ash solid (1 ± 0.001 g) was weighed in an HDPE bottle and then 20 g (±0.001 g) of distilled de-ionized water were carefully introduced into the bottle. Magnetic stirring bars and a Thermix stirring hot-plate were used to stir the suspension

continuously at room temperature (18 °C) for 3 h, 6 h, 1 d, 2 d, 3 d and 7 d.

To study the effect of extraction temperature, the suspensions were heated and maintained at 55 °C by using a hot-plate. This extraction was carried out for 3 d, with temperature as the only variable that differed from the previous extraction.

Extraction of coal fly ash collected from various locations

Coal fly ash samples were collected from different locations (labelled STK, CZ1 and SFA and provided by Electric Power Research Institute) and extracted with pH 7 (DDW) and pH 2 (adjusted by diluted HNO_3) solution. The distilled de-ionized water for the extraction was purged with He gas to reduce dissolved O_2 . The extraction process was also kept in a nitrogen atmosphere by introducing nitrogen gas (99.99% purity) and sealing the bottles with parafilm (American National Can, Greenwich, CT, USA). This was done to reduce the possibility of the arsenic oxidation.

All suspensions were filtered by 0.2 μm hydrophilic nylon membrane filters (Alltech, Deerfield, IL, USA). After filtration, the clear solutions were directly introduced into the concentric nebulizer for elemental analysis or were injected into the HPLC column for elemental speciation. All measurements are based on 3 replicate runs.

RESULTS AND DISCUSSION

Fig. 1(a) shows the concentrations of some trace elements in Coal Fly Ash (NIST SRM 1633a) after stirring for 7 d with water at various pH values. Most of them are released in small amounts in water under normal environmental pH conditions ($\text{pH} = 5\text{--}7$). However, when the pH is < 2 or > 11 , the solubilities of trace elements in coal fly ash are markedly increased. At pH 1 and 12, arsenic and vanadium are the most soluble species among those elements under investigation. Even at the pH 1 extracted solution, only about 50% of arsenic and 17% of vanadium (calculation based on their total masses in solution compared with the solid) in coal fly ash solid dissolve in water when compared with the certified values. Fig. 1(b) with an expanded concentration scale further demonstrates the possibility for speciating arsenic (As), vanadium (V), zinc (Zn), nickel (Ni) and manganese (Mn) in the neutral water extracted solutions ($\text{pH} = 7$), since the concentrations of those elements ranging from 10 to 20 ng g^{-1} is within the working range of HPLC-ICP-MS.

The concentrations of chromium (Cr), lead (Pb) and cadmium (Cd) in the neutral water extracted solutions may be too low to be speciated. The trace elements in coal fly ash can exist in various forms such as salts, silicates and oxides. The coal fly ash–water equilibrium system is complex because of various water–solid interactions. These interactions may involve chemical reactions such as precipitation–desorption, complexation, adsorption–desorption and oxidation–reduction, although precipitation–desorption was found to be a dominant reaction for Cr compounds.²² In a simplest case, for example, As_2O_3 and As_2O_5 are assumed to exist in the coal fly ash solid phase. The solubility of these oxides in aqueous media depends mainly on their hydrolytic behaviour.

It is known that both As_2O_3 and As_2O_5 are soluble in water, although the solubility of As_2O_5 is about 6 times higher than that of As_2O_3 .²³ An acidic or basic solution increases the trace element solubility, as the addition of H^+ or OH^- forces the equilibrium to form more water-soluble species. It is understandable that the concentration of As in the extracted solution depends on the total amount of As, the As species concentrations in the coal fly ash and the extraction pH.

The pH-dependent behaviour is likely for other elements as well, although there may be only one chemical form, such as

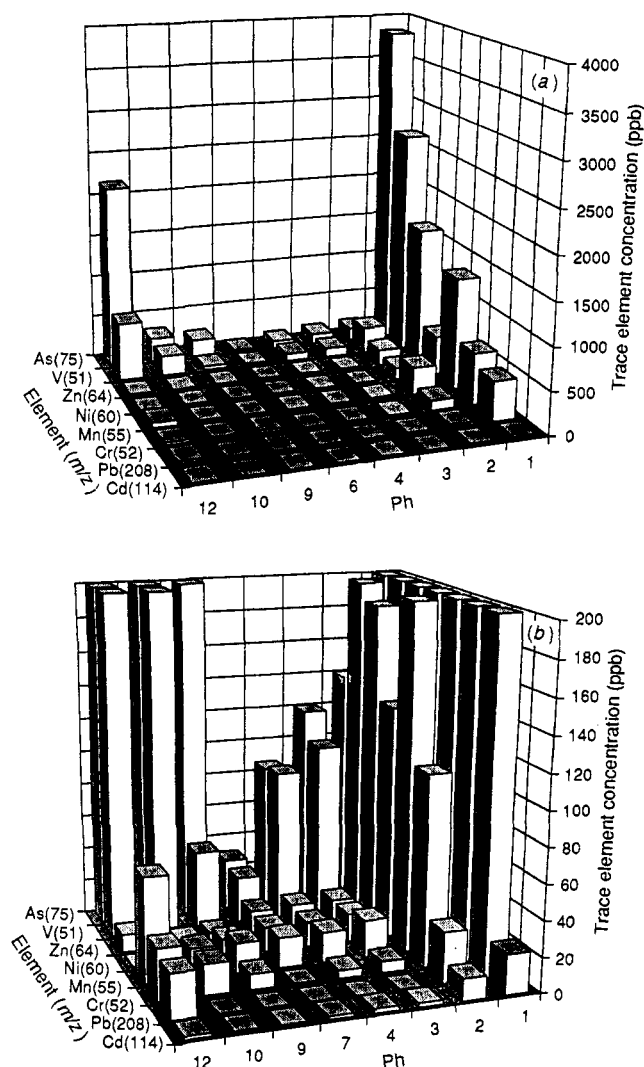


Fig. 1 (a) Effect of varying pH on the solubilities of trace elements in Coal Fly Ash (NIST SRM 1633a). The concentration represents an average from 3 replicate runs. (b) An expanded concentration scale

oxide in the coal fly ash. In addition, as elements are released into aqueous solution, chemical reactions such as oxidation–reduction may take place. For example, at $\text{pH} < 4.8$, only Cr^{III} was found.²² This was believed to be due to Fe^{II} in the solution acting as a reductant for Cr^{VI} . Furthermore, even if no oxidation–reduction takes place, the trace elements released from the solid phase to aqueous phase would change their original form to the hydrolysed species. Based on the above discussion and on the environmental concerns, only the stable hydrolytic species in the coal fly ash–water system were investigated in this work, since only the ‘mobile species’ would give the contamination or pose an environmental or health risk. No attempt has been made to investigate the original (and possibly unavailable) forms in the solid phase or the dissolution reaction mechanism.

The effect of extraction time from a 3 h to 7 d equilibration period at pH 7 on solubilities of trace elements in coal fly ash (NIST 1633a) is shown in Fig. 2. As can be seen, the concentrations for most of the trace elements slightly increase with longer equilibration except Cd, Cr and Pb, suggesting their relative insolubility in the aqueous extracting solutions. For As, however, a plateau between the 3 d and 7 d extraction indicates that maximum extraction (dissolution) has probably been reached. As a result, 3 or 7 d extractions were thought to be reasonable and were used throughout the investigation. The

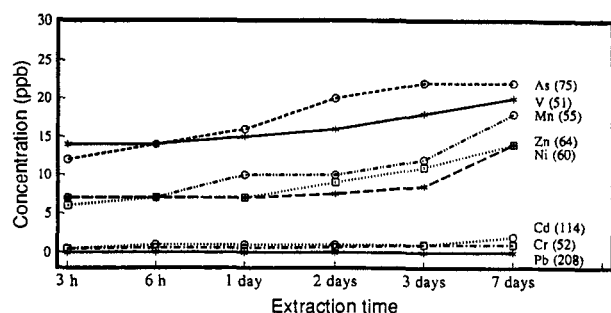


Fig. 2 Effect of dissolution time on the solubilities of trace elements in Coal Fly Ash (NIST SRM 1633a) at pH 7

effect of extraction temperature on the solubilities of trace elements in Coal Fly Ash (NIST SRM 1633a) also was studied by comparing the trace element concentrations in the extracted solution between 18 °C (room temperature) and 55 °C. The results (Fig. 3) show no significant increase in solubility, even though a higher temperature might result in a higher solubility in some cases. Nickel was the only exception, as, at 55 °C, the Ni concentration was found to be about four times higher than that at 18 °C. No explanation for this is available at this time since the precise species are unknown.

Comparisons of trace element solubilities in different types of acidic as well as basic solutions are shown in Fig. 4. No significant difference was observed between HNO₃ and HCl; HNO₃ and H₂SO₄; and NaOH and Na₂CO₃. This means that the potential interference of ⁴⁰Ar³⁵Cl⁺ on ⁷⁵As⁺ as well as ³⁵Cl¹⁶O⁺ on ⁵¹V⁺, due to chloride, can be neglected with these extracted solutions. In addition, the complexation reaction by various acids or bases appears insignificant. The trace element solubilities for coal fly ash depend primarily on the pH of the extracted solution and little on the acid or base used for the studied here.

Fig. 5 shows a chromatogram of As^{III}, DMA, MMA, and As^V, spiked with 500 ppm NaCl. As can be seen, the chloride appearing as ⁴⁰Ar³⁵Cl⁺ after about 6 min can be completely separated from all arsenic species, (*m/z* = 75). Therefore, soluble Cl⁻ salts commonly should have no effect on arsenic speciation with this HPLC-ICP-MS procedure.

The initial neutral water extraction study^{24,25} for arsenic speciation in NIST SRM 1633a by HPLC-ICP-MS shows As^V (≈ 20 ng g⁻¹) as the predominant species (by comparison with standard retention times) with a small amount (≈ 0.2 ng g⁻¹) of As^{III} [Fig. 6(a)]. Fig. 6(c)–(e) shows the neutral extraction-speciation with grinding and sonication and will be discussed below. By contrast, only As^V was found at increased concen-

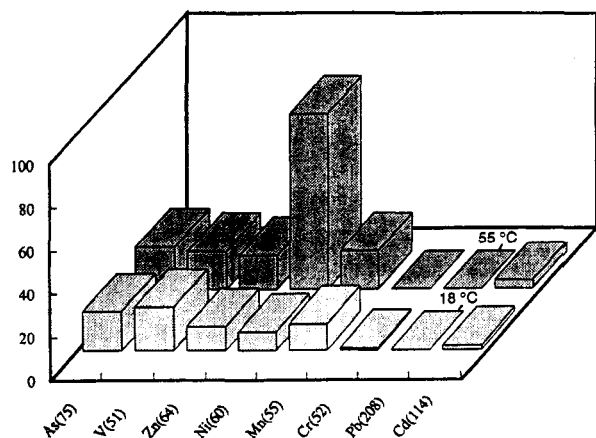


Fig. 3 Effect of dissolution temperature on the solubilities of trace elements in Coal Fly Ash (NIST SRM 1633a) at pH 7

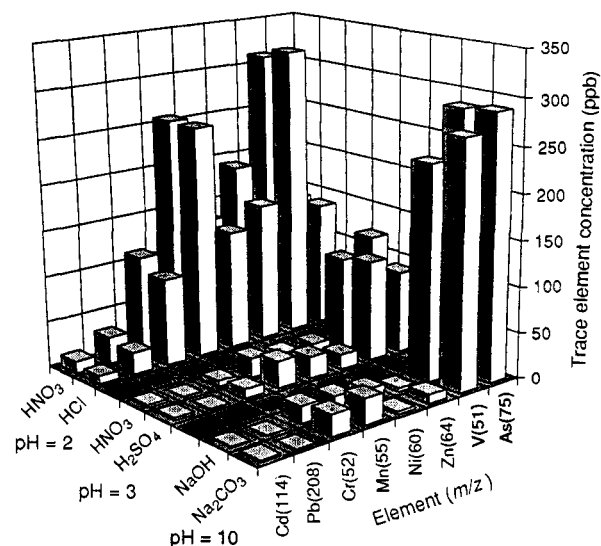


Fig. 4 Comparison of trace element solubilities in different acidic and basic solutions

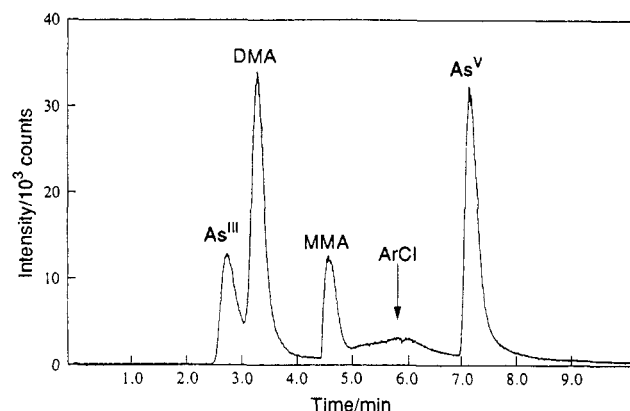


Fig. 5 Speciation of a mixed standard solution of As^{III}, As^V, DMA and MMA, each at 50 ppb, spiked with 500 ppm of NaCl. Chromatographic conditions are given in the text

tration at pH 2 [Fig. 6(b)]. A conversion from As^{III} to As^V might have taken place during the acidic extraction process with oxidizing agents, *e.g.*, O₂ from the atmosphere, or high oxidation state elements in the extracted solution such as Mn or Cr. The reduction potentials of these oxidizing agents are usually higher in acidic than neutral aqueous media. These early observations suggested neutral pH and an O₂-free conditions for the extraction of arsenic to minimize conversion from As^{III} to As^V. However, when the same extracted solution, was analysed again by HPLC-ICP-MS after five months storage, there was no significant change, intimating that atmospheric O₂ is not the likely oxidizing source for arsenic, or more conversion would have been noted as the solution aged. To study the effect of oxygen, an extracted solution from coal fly ash (CZ1) containing significant amounts of As^{III} and As^V was analysed. It was found that CZ1 released about 12 ng g⁻¹ of As^{III} and 230 ng g⁻¹ of As^V in the neutral water extracted solution without de-gassing or other treatment. By comparing the results from the same extraction period with de-gassing and with N₂ atmosphere, no significant difference was found. This further indicated that O₂ has little part in As^{III} to As^V conversion.

The extracted solutions from both coal fly ash CZ1 and NIST SRM 1633a at pH 7 were acidified to pH 1 and then injected into the HPLC-ICP-MS system for further study. No obvious decrease in As^{III} or increase in As^V was found.

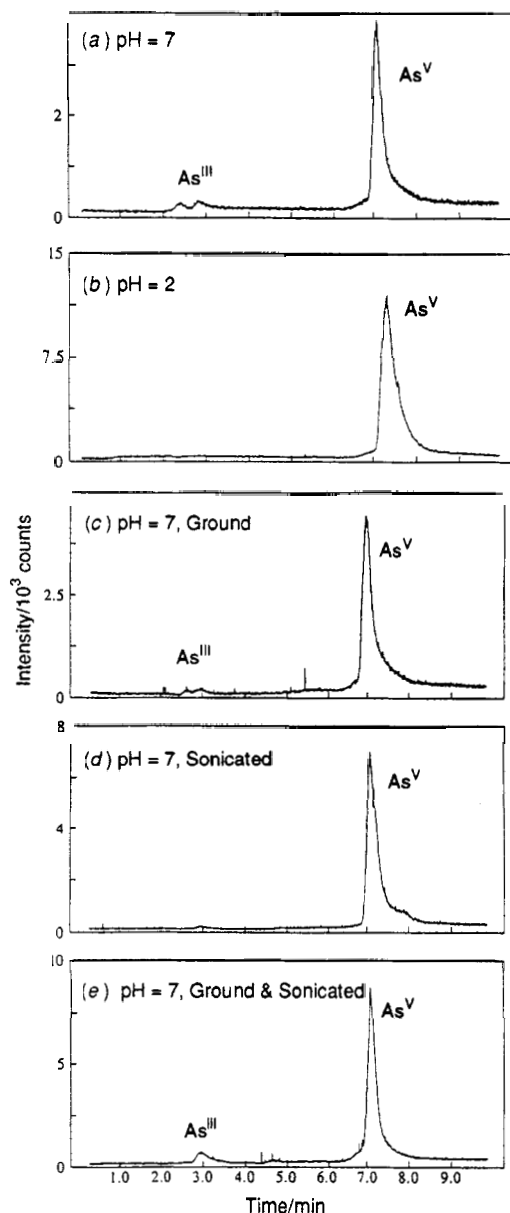


Fig. 6 Speciation of arsenic in dissolved solutions from Coal Fly Ash (NIST SRM 1633a); Chromatographic conditions same as Fig. 5. (a) Extraction solution at pH 7; (b) extraction solution at pH 2; (c) extraction solution at pH 7 with grinding; (d) extraction solution at pH 7 with ultra-sonication; and (e) extraction solution at pH 7 with both grinding and ultra-sonication

However, this finding does not preclude the possibility of As^{III} oxidation by other elements in high oxidation states, since those element concentrations at pH 7 may not be sufficient to convert such As^{III} to As^{V} . The overall chemistry differences from extraction at pH 1 compared with extraction from neutral water, then acidified to pH 1, would be expected to be different. Further investigation is needed to provide confirmation for As^{III} oxidation by high oxidation state elements in the fly ash.

The effect of pH on the speciation of nickel was also performed using the method developed by Tomlinson *et al.*²⁰ as shown in Fig. 7. At a pH of 2 at m/z 58, 255 ppb of nickel was extracted. At a pH of 9, 39.7 ppb was extracted and at a pH of 12, 16.9 ppb was seen. When the fly ash sample, SFA, was speciated at pH 2 and 7, an additional peak appeared at pH 2 which could be due to a polyatomic interferer from calcium. At a pH of 7, 343 ppb of Ni^{II} was seen and a signal equalling an amount of 289 ppb Ni was determined at a pH of 2.

Fig. 8(a) shows the speciation of vanadium at m/z 51

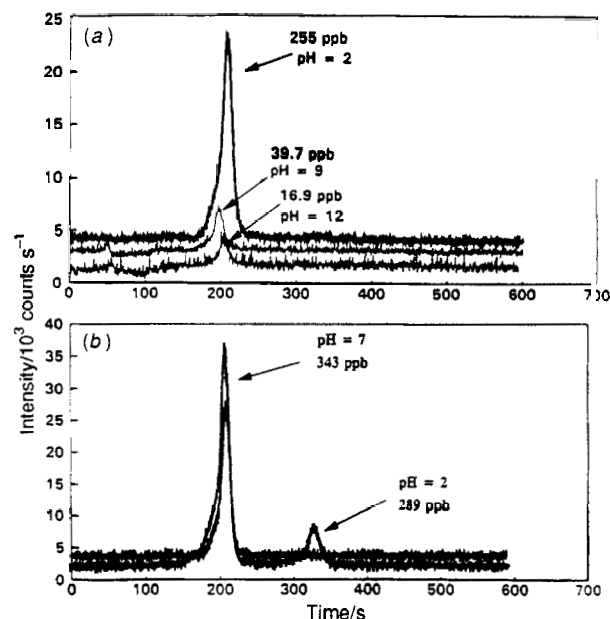


Fig. 7 (a) Speciation of nickel from Coal Fly Ash (NIST SRM 1633a) and (b) speciation of nickel in sample SFA. Mobile phase contained 6 mmol l^{-1} 2,6-pyridinedicarboxylic acid and 8.6 mmol l^{-1} lithium hydroxide adjusted to a pH of 6.8 with ammonium hydroxide; Flow rate used for the separation was 1.5 ml min^{-1}

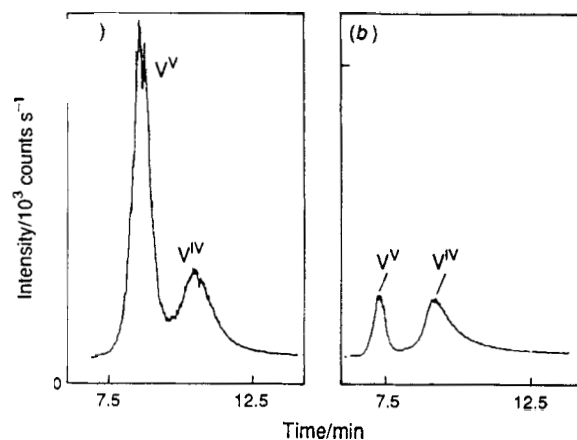


Fig. 8 (a) Speciation of vanadium extraction solution at pH 1 from Coal Fly Ash (NIST SRM 1633a) and (b) chromatogram of a vanadium standard solution. Mobile phase contained 6 mmol l^{-1} 2,6-pyridinedicarboxylic acid and 8.6 mmol l^{-1} lithium hydroxide adjusted to a pH of 3.6 with nitric acid solution

extracted at pH 1 and adjusted to a pH of 2.6 for the chromatography.²⁰ Fig. 8(b) shows the vanadium(IV) and vanadium(V) standards on the same scale as the unknowns from SFA. The vanadium and nickel results suggest that other elements can be extracted and speciated.

Extraction at pH 7 was done with and without grinding-ultra-sonicating. Grinding and ultrasonication should improve the extraction efficiency since it theoretically provides more efficient contact between fresh solvent and solid surfaces from the greater surface area of finely divided particles. Fig. 9 illustrates the effect of grinding and ultra-sonicating on the solubilities of trace elements in Coal Fly Ash NIST SRM 1633a at pH 7. The solubilities of most of the trace elements under investigation were increased by various degrees with grinding and/or ultra-sonication except with Cr and Pb. Among them, Mn showed the greatest improvement in the extraction efficiency.

In digestion procedures, ideally all solids would dissolve,

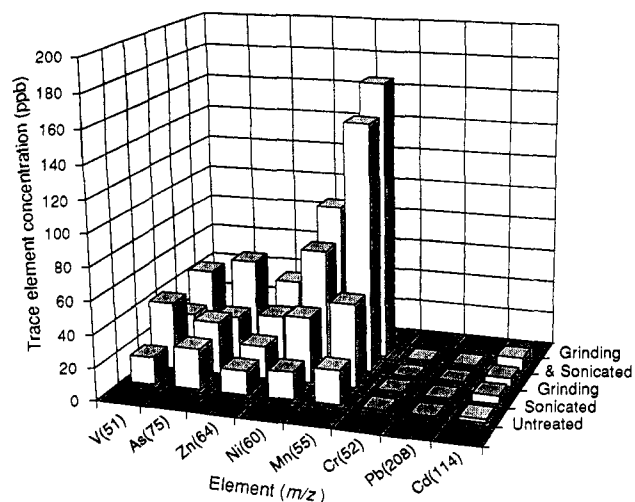


Fig. 9 Effect of grinding and sonicating on solubilities of trace elements in Coal Fly Ash (NIST SRM 1633a) at pH 7

while in extraction, the solubility of the solid compound depends in part on solid surface availability and solubility rather than harsh chemical reaction. If the trace element compounds in the fly ash are not homogeneously distributed on the particle surface, different results from one extraction to another will be expected. It is seen from Fig. 6(a)–(e) that the intensity of As^{V} increases with grinding and sonicating, or with a lower pH, as might be expected from surface area and solubility considerations. The concentration of As^{III} , however, is unpredictable and may depend on the sample batch. Sample batch dependent behaviour for As^{V} may also have an effect, but it is not apparent at the higher As^{V} concentration. Thus, particle surface homogeneity is a concern with aqueous extractions of fly ash, as would be expected.

Possible inconsistencies in As^{III} results can be found in Fig. 6(a)–(e). It was previously indicated that grinding and sonicating should improve the extraction efficiency for both As^{V} and As^{III} because of more effective contact between solvent enhanced surface areas. Higher concentrations of both As^{V} and As^{III} in the extracted solution should be expected. However, Fig. 6(a) and (c)–(e) shows increasing amounts of As^{V} and small but varying amounts of As^{III} from neutral water extracted solutions with grinding, sonicating or both, although the amounts are small and near the low working range of the technique.

Coal fly ash sample STK was used to study further this arsenic conversion since a relatively large amount of As^{III} was found in this sample. The arsenic speciation chromatograms of extracted solutions at pH 7 from sample STK with and without grinding are illustrated in Fig. 10 and an increase in As^{V} and a decrease in As^{III} with 24 h grinding can be seen. This confirms that arsenic conversion did occur. The conversion is probably promoted by the grinding process, which may result in more high oxidation state elements in the extracted solution. The possibly inconsistent results from Fig. 6(a) and (c)–(e) may be caused by several factors. Grinding and sonicating improves the extraction efficiency for both As^{V} and As^{III} and more arsenic will be released into the extracted solution; however, with grinding and sonicating other elements with high oxidation states are extracted at the same time, potentially resulting in more conversion from As^{III} to As^{V} . The processes are competitive, but not easily predictable without much more being known about the sample. Non-homogeneous distribution on the surface of coal fly ash particles will also influence the extraction of differing arsenic species, and may, therefore, cause uncertainty in As^{III} results. Results at the low working range for the speciation studies also have larger uncertainties.

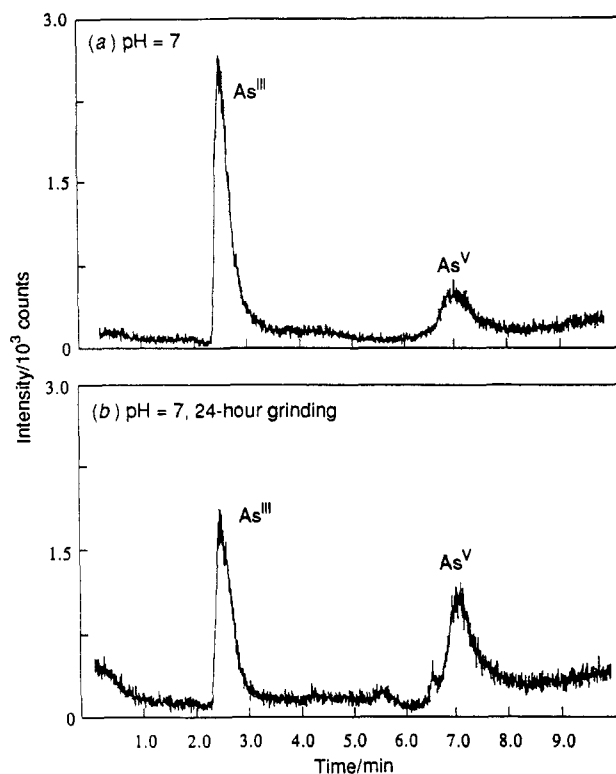


Fig. 10 Speciation of arsenic in dissolved solution from coal fly ash STK: (a) extraction solution at pH 7; and (b) extraction solution pH 7 with grinding

Fig. 11(a) shows a small amount of As^{III} and a dominant amount of As^{V} extracted at pH 7 from SFA, but an increasing amount of As^{III} with a basically constant amount of As^{V} at pH 2 [Fig. 11(b)]. These results differ somewhat from those of NIST SRM 1633a and may be due to the differing nature

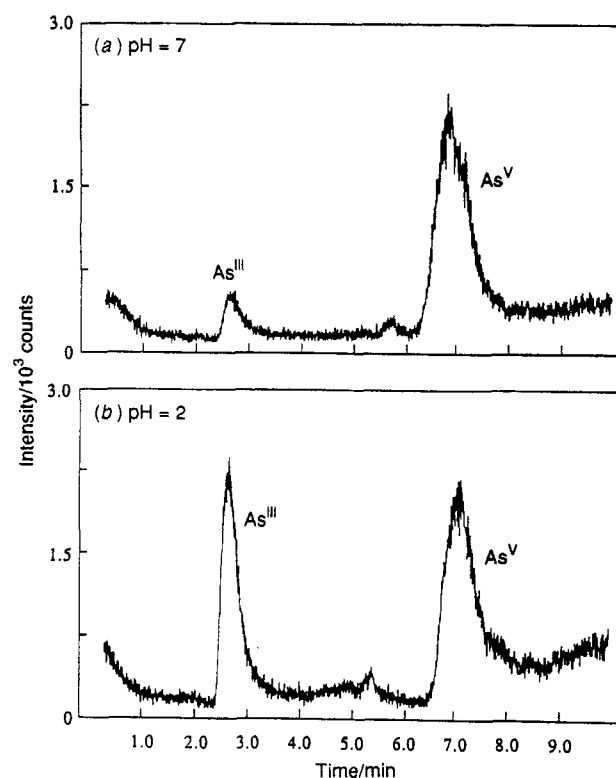


Fig. 11 Speciation of arsenic in extraction solution from coal fly ash SFA: (a) extraction solution at pH 7; and (b) extraction solution at pH 2

of arsenic species in the coal fly ash solid. Sample SFA may contain more As^{III} and clearly more was extracted at lower pH. Arsenic conversion in these samples may be dependent on the nature and amount of co-existing high oxidation state elements. Furthermore, the elemental species profiles for any coal fly ash samples are highly dependent on original coal starting materials, combustion conditions, etc. and therefore must be determined on a case-by-case basis until a broader data base is assembled.

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REFERENCES

- 1 Fowler, B. A., *Biological and Environmental Effect of Arsenic*, Elsevier, New York, 1983.
- 2 Hodgson, E., Mailman, R. B., and Chambers, J. E., *Dictionary of Toxicology*, Macmillan, London, 1988, 40–41.
- 3 Snow, E. T., and Xu, Li-Sha, *Biological Trace Element Research*, 1989, vol 21, 61–71.
- 4 Krull, I. S., Bushee, D., Savage, R. N., Schleicher, R. G., and Smith, S. B., Jr., *Anal. Lett.*, 1982, **15**, 267.
- 5 Willsky, G. R., White, D. A., and McCabe, B. C., *J. Biol. Chem.*, 1984, **259**, 13273.
- 6 Sheppard, B. S., Caruso, J. A., Heitkemper, D. T., and Wolnik, K. A., *Analyst*, 1992, **117**, 971.
- 7 Sheppard, B. S., Shen, W. L., Caruso, J. A., Heitkemper, D. T., and Fricke, F. L., *J. Anal. At. Spectrom.*, 1990, **5**, 431.
- 8 Heitkemper, D. T., Creek, J., Caruso, J. A., and Fricke, F. L., *J. Anal. At. Spectrom.*, 1989, **4**, 279.
- 9 Larsen, E. H., Pritzl, G., and Hansen, S. H., *J. Anal. At. Spectrom.*, 1993, **8**, 557.
- 10 Hansen, S. H., Larsen, E. H., Pritzl, G., and Cornett, C., *J. Anal. At. Spectrom.*, 1992, **7**, 629.
- 11 Beauchemin, D., Siu, K. W. M., McLaren, J. W., and Berman, S. S., *J. Anal. At. Spectrom.*, 1989, **4**, 285.
- 12 Branch, S., Ebdon, L., and O'Neill, P., *J. Anal. At. Spectrom.*, 1994, **9**, 33.
- 13 Morita, M., Uehiro, T., and Fuwa, K., *Anal. Chem.*, 1981, **53**, 1806.
- 14 Morita, M., and Shibata, Y., *Anal. Sci.*, 1987, **3**, 575.
- 15 Roychowdhury, S. B., and Koropchak, J. A., *Anal. Chem.*, 1990, **62**, 484.
- 16 Spall, W. D., Lynn, J. G., Andersen, J. L., Valdez, J. G., and Gurley, L. R., *Anal. Chem.*, 1986, **58**, 1340.
- 17 Low, G. K.-C., Batley, G. E., and Buchanan, S. J., *J. Chromatogr.*, 1986, **386**, 423.
- 18 Nisamanepong, W., Ibrahim, M., Gilbert, W., and Caruso, J. A., *J. Chromatogr., Sci.*, 1984, **22**, 473.
- 19 Nakata, F., Hara, S., Matsuo, H., Kumamaru, T., and Matsushita, S., *Anal. Sci.*, 1985, **1**, 157.
- 20 Tomlinson, M., Wang, J., and Caruso, J. A., *J. Anal. At. Spectrom.*, 1994, **9**, 957.
- 21 Hirayama, S., Kageyama, S., and Unohara, N., *Analyst*, 1992, **117**, 13.
- 22 Rai, D., and Szelmezcza, R. W., *J. Environ. Qual.* 1990, **19**, 378.
- 23 *CRC handbook of Chemistry and Physics*, CRC press, Cleveland, OH.
- 24 Wang, J., Tomlinson, M., and Caruso, J. A., presented at the 41st ASMS (American Society for Mass Spectrometry) conference, San Francisco, CA, USA, June, 1993, paper No. 628.
- 25 Caruso, J. A., Tomlinson, M., and Wang, J., presented at the 20th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Detroit, IL, USA, October 1993, paper No. 343.

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