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# Determination of inorganic oxyanions of As and Se by HPLC–ICPMS

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**Abstract**

A liquid chromatographic separation of inorganic oxyanions of As (As(V) and As(III)) and Se (Se(VI) and Se(IV)) using mixed ion-pairing reagents followed by ICPMS detection is described. The separation was accomplished in less than 4 min on Capcell C18 RP column using mixed ion-pairing modifier containing 5 mM of butane sulfonic acid (BSA), 2 mM malonic acid, 0.30 mM hexane sulfonic acid (HSA) and 0.5% methanol of pH 2.5. All four species were resolved with retention times of 2.4, 2.6, 3.0, and 3.1 min for Se(VI), As(V), As(III), and Se(IV), respectively. The detection limits were less than 0.08 and 0.77 $\mu g\,l^{-1}$ for arsenic and selenium species, respectively. The relative standard deviation of the proposed method for arsenic (at 2.5 $\mu g\,l^{-1}$) and selenium (at 10 $\mu g\,l^{-1}$) was less than 3.7 and 4.8%, respectively. The technique was used to determine inorganic oxyanions of As and Se in water samples (tap, well, and river) and extracts of coal fly ash and sediment. Low power microwave digestion was employed for extraction from fly ash and sediment samples.


*Keywords:* Arsenic; Selenium; Ion-pair chromatography; ICPMS; Coal fly ash; Sediment

## 1. Introduction

The health effects of trace elements are often dependent upon both the quantities and chemical forms of the element. Arsenic and selenium are potential toxic elements that are found in the environment [1,2]. As for arsenic, the two most toxic species are arsenite (As(III)) and arsenate (As(V)), respectively, which represent the main forms of arsenic present in soils, sediment and waters [3]. In the case of selenium, it is an essential nutrient at low levels of intake and produce toxic symptoms when it is ingested at levels higher than those required for adequate nutrition [4]. The narrow concentration range between the two opposing effects requires accurate and precise knowledge of selenium species present in the environment. In natural waters, coal fly ash and soils, selenium exist predominantly in two inorganic forms which are more toxic than organic species [5,6]. Studies over the years on arsenic and selenium speciation have clearly demonstrated the importance of chemical speciation.

Over the past 10 years, considerable advances have been made in speciation analysis through the application of coupled or hyphenated techniques. Detection system involving ETAAS [7] can only be used "off-line". While HG techniques [8,9] require post column treatment of analytes because of different reduction characteristics of As(III) and As(V). Both ICP-OES and ICPMS offer on-line detection with little sample manipulation after the separation. The use of ICPMS detection after chromatographic separation offers excellent detection limits and multi-element capability.

Jackson and Miller [10] described ion chromatographic separation and ICPMS detection of oxyanions: As and Se. The separation was accomplished in 7 min and detection limits for this separation were 0.072 $\mu g\,l^{-1}$ As(III), 0.284 $\mu g\,l^{-1}$ As(V), 0.868 $\mu g\,l^{-1}$ Se(IV), and 1.174 $\mu g\,l^{-1}$ Se(IV) for 100 $\mu l$ injection volume. This technique was used to determine inorganic As and Se species in various coal fly ash samples. Multi-element speciation of As, Se and Cr using HPLC–ICPMS is reported by Martinex-Bravo et al. [11]. The separation of seven species was achieved in 14 min using gradient elution with $NH_4NO_3$ at different

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molar concentration. Detection limits are 40–60 ng $l^{-1}$ for arsenic species and 1.2–1.4 μg $l^{-1}$ for selenium species. In the ion-pair chromatography, alkyl sulphonates in the pH range of 2–4 were reported for the separation of As and Se species [12,17]. However, the selection of number of carbons in the ion-pair modifier is important in order to achieve proper separation among MMA, DMA, and AB. This is due to the difference in hydrophobicity and their interaction with C18 stationary phase. Le et al. [12] proposed elevated temperature liquid chromatography separation of As and Se with ICPMS detection and applied to tuna fish extracts. The entire separation was completed in 19 min at 70 °C column temperature. A narrow bore liquid chromatographic method was proposed by Woller et al. [13] for the separation of inorganic As and Se. In this technique, the separation time was shortened and better detection limit, $<0.04$ μg $l^{-1}$ was achieved using MCN-ICPMS.

In the present report, we propose a rapid method of liquid chromatographic separation using mixed ion-pairing reagents and ICPMS detection of inorganic arsenic and selenium species. The advantage of the proposed method is that the separation time was shortened to less than 4 min and detection limits are improved with 25 μl injection volume. The technique was applied to determine inorganic arsenic and selenium species in fresh water samples and extracts of coal fly ash and sediments.

## 2. Experimental

### 2.1. Instrumentation

A Perkin-Elmer Elan 6000 ICPMS instrument (Perkin-Elmer SCIEX, Concord, Ontario, Canada) with concentric nebulizer and cyclonic chamber was used as a detector for chromatographic separations and for total element analysis of extracts and wet digests of fly ash and sediment samples. The operating conditions for ICPMS are shown in Table 1. Prior to chromatographic separations, conventional sample introduction via Gilson peristaltic pump was used to optimize the instrument to maximize the signal intensity at mass/charge (*m*/*z*) 75. A 10 μg $l^{-1}$ As was used to optimize nebulizer gas flow and lens voltage for maximum intensity. It was assumed that the maximum lens voltage at *m*/*z* 75 would also be appropriate for monitoring Se at *m*/*z* 77.

A Dionex model DX-100 HPLC system with Rheodyne model 9125 six port injection and a 25 μl loop was used. A Capcell PAK C18 (250 mm × 4.6 mm i.d.) from m/s Shiseido Co. Ltd., Tokyo, Japan was used for separation of As and Se species. The end of the analytical column was connected to concentratic nebulizer by a 20 cm length PEEK tubing coupled to a 12 cm length polyethylene tubing (0.575 i.d. and 0.95 o.d.). A mixture of 5 mM butane sulfonic acid (BSA)–2 mM malonic acid–0.3 mM hexanesulfonic acid (HSA) of pH 2.5 was used as an eluent. A 0.5% of methanol was maintained in the eluent mixture all the time. A flow rate of 1 ml $min^{-1}$ was used throughout the experiment.

Table 1
Operating conditions for ICPMS and IC instruments

| | |
|---|---|
| ICPMS | |
| Rf forward power (W) | 1200 |
| Plasma gas flow rate (l $min^{-1}$) | 15 |
| Nebulizer gas flow rate (l $min^{-1}$) | 0.80–0.90 |
| Lens voltage (V) | 13 |
| Monitoring masses (*m*/*z*) | $^{75}$As, $^{77}$Se |
| Dwell time per unit (ms) | 500 |
| Sweeps per reading | 1 |
| Readings per replicate | 250 |
| Replicates | 1 |
| Total sampling time (min) | 6.00 |
| HPLC | |
| C18 reversed phase column | CAPCELL C18 PAK (250 mm × 4.6 mm i.d.) |
| Mobile phase | 5 mM butanesulfonic acid–2 mM malonic acid–0.3 hexanesulfonic acid–0.5% methanol |
| Flow rate | 1.0 ml $min^{-1}$ |
| Injection volume | 25 μl |

The raw data from Elan 6000 software was later transferred into Total Chrom work station (version 6.02) separately for $^{75}$As and $^{77}$Se to evaluate retention time, peak area and peak heights. Peaks were identified according retention time and confirmed by using standard addition of arsenic and selenium compounds. The arsenic and selenium concentrations in the real samples were quantified via peak areas on the basis of calibration curves of the known forms.

### 2.2. Reagents and standard solutions

For the preparation of reagents and standards, Milli-Q water (18.3 MΩ) was used. All reagents were of analytical grade.

Sodium arsenite of Kanto Chemicals Co. Inc., Japan, and sodium arsenate hyptahydrate, sodium selenite, sodium selenate of Wako Pure Chemical Industries, Japan were used to prepare 1000 mg $l^{-1}$ stock solutions (as elemental As and Se). Daily working standards were prepared by serial dilution of stock solutions. Multi-species mixed standards were used for calibration of IC–ICPMS system.

### 2.3. Microwave extraction of coal fly ash and sediment for As and Se speciation

Low power microwave extraction was successfully applied for arsenic extraction from various sediment and soil samples [17,18]. Therefore, we have employed low power microwave extraction for coal fly ash and sediment samples. Two samples of coal fly ash and sediment were used in this study. An aliquot of ∼100 mg sample was weighed in triplicate into Teflon vessels. Then 10 ml of water or 1 mM

$H_3PO_4$ was added. These samples were digested under closed system using low power microwave setting (50 W, 10 min). After cooling the samples centrifuged at 2500 rpm for 15 min and the supernatant liquid was filtered through 0.45 mm Millipore filter. These extracts were refrigerated at 4 °C and analyzed within 24 h. The total soluble As and Se were determined by direct ICPMS and a 25 μl aliquot of the extract was injected into HPLC–ICPMS system under the proposed condition for speciation analysis.

### 2.4. Total arsenic and selenium in coal fly ash and sediment

For this, 0.2 g of sediment or coal fly ash was treated with 5 ml of HF and 3 ml of aqua regia and digested under closed microwave system (2 min, 250 W; 0.5 min, 0 W; 5 min, 300 W; 0.5 min, 0 W; 5 min, 450 W; 0.5 min, 0 W; 5 min, 600 W; 10 min, 0 W). After cooling, excess of HF was volatilized by the addition of 25 ml of saturated $H_3BO_3$ and then diluted to 50 ml with Milli-Q water. These digests were analyzed for total As and Se by HG-AAS.

## 3. Results and discussions

Arsenic at *m*/*z* 75 and selenium at *m*/*z* 77 were monitored during the chromatographic separation. Due to the fact that the major isotopes of Se at *m*/*z* 78 (23.8%) and 80 (49.6%) are subjected to severe interference from the argon dimmers $^{40}Ar^{38}Ar^{+}$ and $^{40}Ar_2{}^{+}$, se isotopes $^{77}Se$ and $^{82}Se$ are normally used for ICPMS determination [14]. In our case, a better signal-to-background ratio was obtained using *m*/*z* 77 instead of commonly used *m*/*z* 82. Nevertheless, the chloride concentrations should be controlled to avoid the spectral interferences such as $^{40}Ar^{35}Cl$ and $^{40}Ar^{37}Cl$. The effect of chloride concentrations is discussed separately.

### 3.1. Chromatographic separation

Alkylsulfonate ion-pairing modifiers at lower pH values were successfully applied for arsenic and selenium speciation studies. The separation process often depends upon hydrophobicity of the ion-pairing agent and its interaction with C18 stationary phase. In the preliminary studies, we have investigated 5 mM butanesulfnoic acid (BSA) for the separation of As(III), As(V), Se(IV), and Se(VI) at pH 3.0 on a Capcell C18 column. The resulted chromatogram is shown in Fig. 1a. It could be noted all four compounds were separated except that Se(IV) shows partial retention. The change of pH of the mobile phase in the range of 2.5–4.0 did not improve the elution of Se(IV). Subsequently, a mixed ion-pairing agent containing butanesulfonic acid 5 mM and malonic acid, 2 mM at pH 3.0 was examined. The resulted chromatogram is shown in Fig 1b, indicating improvement in the resolution between Se(VI) and Se(IV). Due to high p*K* value of Se(IV), the addition of di-ionic ion-pairing agent has apparently helped for better resolution of Se(IV). Under this condition, it was observed that DMA and AB were co-eluted. An addition of 0.3 mM of hexanesulfonic acid into the eluent mixture has resulted in separation of AB from DMA. This is due to increase in hydrophobicity of these sulfonates with number of carbon in the chain that has helped for resolution [12]. A pH 2.5 was chosen for improving the resolution between As(III) and MMA. It is well known that the addition of carbon (as methanol) to aqueous solution improves the ionization efficiency in plasma [15,16]. For that reason, 0.5% (v/v) methanol was added to eluent mixture

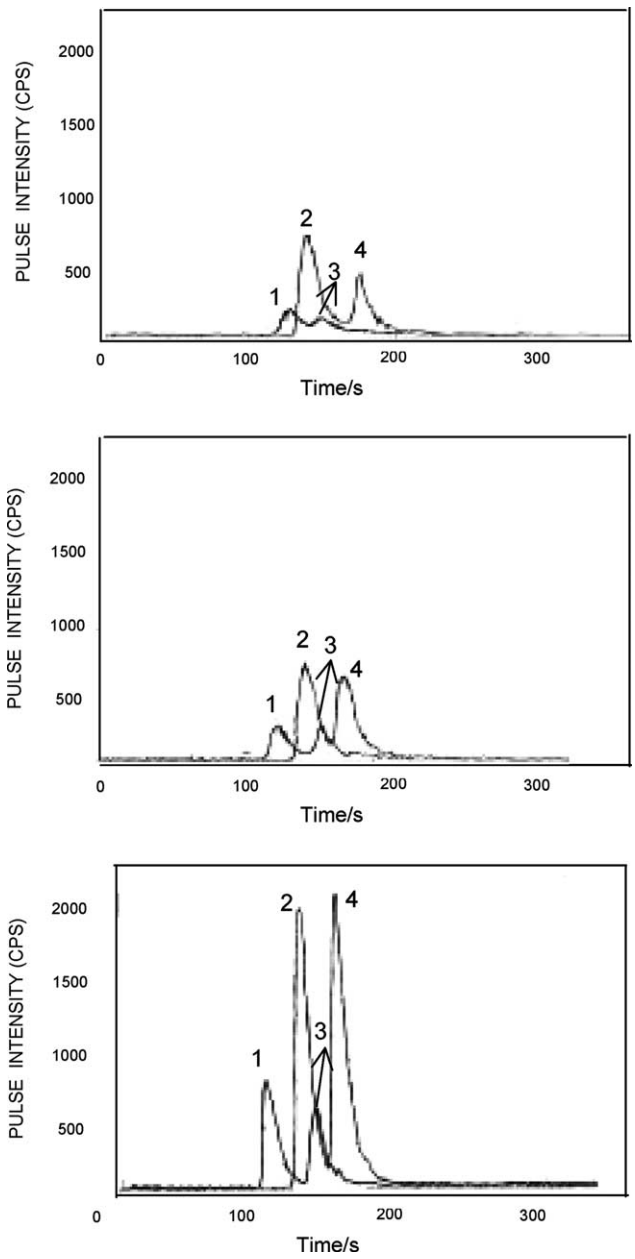


Fig. 1. HPLC–ICPMS chromatogram of arsenic (5 μg $l^{-1}$) and selenium (25 μg $l^{-1}$) standards. (a) BSA 5 mM (pH 3.0) and (b) BSA (5 mM)–malonic acid (2 mM) (pH 3.0) (c) BSA (5 mM)–malonic acid (2 mM)–HSA (0.3 mM)–0.5% methanol (pH 2.5). Peaks are labeled as (1) Se(VI), (2) As(V), (3) Se(IV) and (4) As(III).

which improved the peak intensities by 2–4-fold for all four species (cf. Fig. 1c).

### 3.2. Analytical characteristics

After optimizing the chromatographic parameters, the analytical characteristic of the method was evaluated for each arsenic and selenium species (cf. Table 2). An eight-point calibration was carried out in the concentration range of 1–100 $\mu g\,l^{-1}$ As and 2.5–200 $\mu g\,l^{-1}$ Se, respectively for which the $r^2$ values from least square method was better than 0.997 for all four species. The detection limit was calculated based on $3\sigma$ of the blank intensities at respective retention time and were less than 80 and 0.77 $\mu g\,l^{-1}$ for As and Se, respectively. These figures are comparatively better than earlier reported values [10–12]. The standard addition in the order of 6 s (LOQ) into sample extracts produced significant peaks from baseline. The precision of the method was checked by six replicates at 2.5 $\mu g\,l^{-1}$ As and 10 $\mu g\,l^{-1}$ Se and R.S.D. were less than 4.8% for all four species.

### 3.3. Chloride interference

High concentration of chloride can react in the argon plasma and form $^{40}Ar^{35}Cl$ with *m*/*z* 75 and $^{40}Ar^{37}Cl$ with *m*/*z* 77. To evaluate the possible interference of $Cl^-$ on the chromatographic separation and ICPMS detection, As and Se standards were prepared in a series of NaCl solution (with concentrations of 100, 200, 500, 1000, 2000, and 5000 $mg\,l^{-1}$ $Cl^-$). These were then injected into the HPLC–ICPMS analytical system. Some of the resulted chromatograms are shown in Fig. 2. It was found that there was no effect on the separation of two As species and Se species when $Cl^-$ concentration was less than 2000 $mg\,l^{-1}$. However, As(V) and Se(VI) were co-eluted with chloride ion when Cl concentration exceeds 2000 $mg\,l^{-1}$. The appearance of ArCl peak could be seen when Cl concentration in the range of 1000–2000 $mg\,l^{-1}$ (cf. Fig. 2b and c). Therefore, the chloride concentrations should be controlled to less than 1000 $mg\,l^{-1}$ in order to avoid interference due to ArCl.

### 3.4. Applications

The recommended HPLC–ICPMS procedure was applied to simultaneous determination of inorganic oxyanions of As and Se in water samples and extracts of coal fly ash and sediment.

#### 3.4.1. Water samples

A river water (Hiroshima, Japan), well water (Kumamoto, Japan) and a tap water samples were analyzed by the proposed procedure. These water samples were filtered through 0.45 μm membrane filter and stored at 4 °C until analysis. Analysis was carried out with in 24 h of sample collection to avoid the inter-conversions. The results are given in Table 3. As(V) was found in all samples (between 0.17 and 0.64 $\mu g\,l^{-1}$ As) while As(III) was present only in river and well waters (0.13–0.19 $\mu g\,l^{-1}$ As). Selenium species concentrations were below the detection limit. Hence, spiking experiment was carried out in three replicates for all four species and recoveries were in the range of 98–102%.

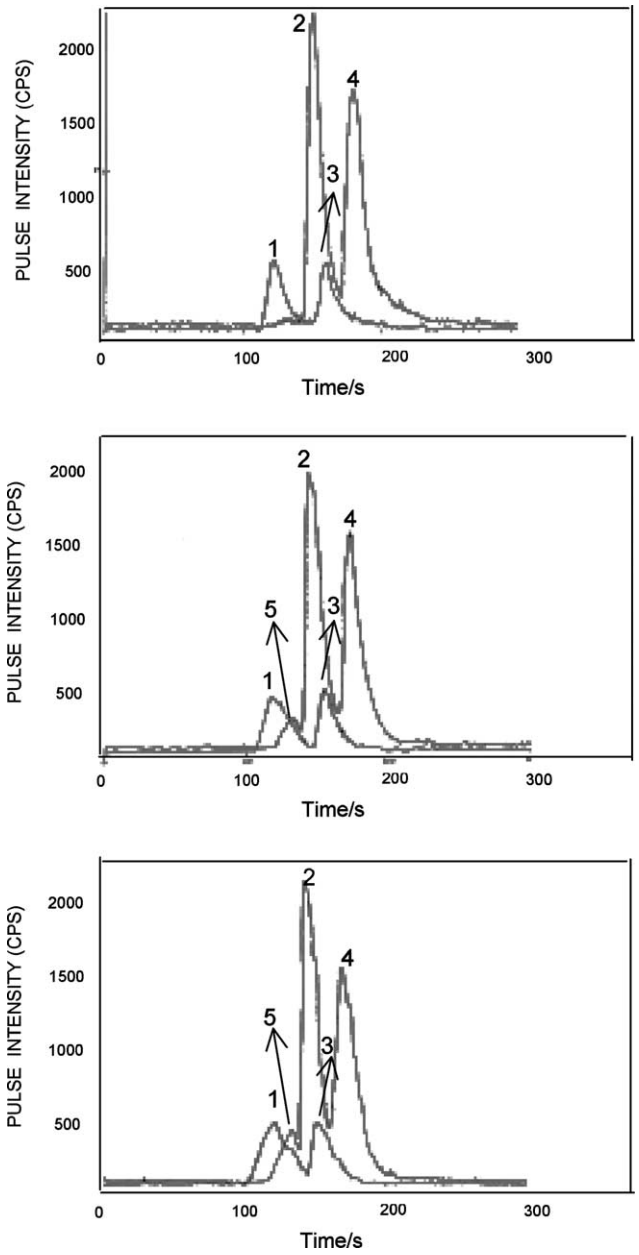


Fig. 2. Effect of chloride concentration on the chromatographic separation of arsenic (5 $\mu g\,l^{-1}$) and selenium (12.5 $\mu g\,l^{-1}$) compounds using eluent mixture of BSA (5 mM)–malonic acid (2 mM)–HSA (0.3 mM)–0.5% methanol (pH 2.5). (a) In the presence of 200 $mg\,l^{-1}$ $Cl^-$, (b) in presence of 1000 $mg\,l^{-1}$ $Cl^-$ and (c) in the presence of 2000 $mg\,l^{-1}$ $Cl^-$. Peaks are labeled as: (1) Se(VI), (2) As(V), (3) Se(IV), (4) As(III) and (5) ArCl.

#### 3.4.2. Extracts of coal fly ash and sediment

The extraction efficiency of the microwave assisted extraction was evaluated determining the ratio between total

Table 2
Analytical merits of HPLC–ICPMS

| Parameter | As(V) | As(III) | Se(VI) | Se(IV) |
|---|---|---|---|---|
| Retention time (min) | 2.4 | 3.0 | 2.6 | 3.1 |
| Linear range ($\mu g\,l^{-1}$) | 0–100 | 0–100 | 0–200 | 0–200 |
| Linear equation | $y = 7197x + 3490$, $R^2 = 0.9994$ | $y = 5576x + 2661$, $R^2 = 0.999$ | $y = 498x + 553$, $R^2 = 0.9973$ | $y = 423x - 554$, $R^2 = 0.9984$ |
| Detection limit ($3\sigma$) ($\mu g\,l^{-1}$) | 0.07 | 0.08 | 0.63 | 0.77 |
| Absolute concentration (pg) | 1.8 | 2.0 | 15.8 | 19.3 |
| Precision (R.S.D. (%)), (As 2.5 $\mu g\,l^{-1}$; Se 10 $\mu g\,l^{-1}$) | 2.7 | 3.7 | 4.8 | 4.8 |

Table 3
As and Se speciation of water samples[a]

| Samples | As(V) ($\mu g\,l^{-1}$) | | As(III) ($\mu g\,l^{-1}$) | | Se(VI) ($\mu g\,l^{-1}$) | | Se(IV) ($\mu g\,l^{-1}$) | |
|---|---|---|---|---|---|---|---|---|
| | Standard addition | Amount found | Standard addition | Amount found | Standard addition | Amount found | Standard addition | Amount found |
| River water | – | 0.17 ± 0.03 | – | 0.13 ± 0.03 | – | <0.63 | – | <0.77 |
| | 0.25 | 0.43 ± 0.03 | 0.25 | 0.37 ± 0.03 | 2.5 | 2.40 ± 0.07 | 2.5 | 2.50 ± 0.06 |
| | 0.50 | 0.67 ± 0.02 | 0.50 | 0.53 ± 0.03 | 5.0 | 5.10 ± 0.06 | 5.0 | 5.00 ± 0.04 |
| Well water | – | 0.64 ± 0.03 | – | 0.19 + 0.02 | – | <0.63 | – | <0.77 |
| | 0.25 | 0.87 ± 0.03 | 0.25 | 0.42 ± 0.05 | 2.5 | 2.6 ± 0.07 | 2.5 | 2.8 ± 0.07 |
| Tap water | – | 0.17 ± 0.04 | – | <0.08 | – | <0.63 | – | <0.77 |
| | 0.25 | 0.41 ± 0.03 | 0.25 | 0.24 ± 0.05 | 2.5 | 2.5 ± 0.04 | 2.5 | 2.6 ± 0.06 |

[a] Average of triplicates.

arsenic in the microwave extract and acid wet digests (cf. Table 4). The diluted $H_3PO_4$ media has obtained better extraction efficiency than water alone for As which is in good agreement with earlier reports [17,18]. However, there is no significant difference in the case of Se extraction. This may be due to difference in mobility of the individual species. It can be seen from the table, the recovery is 90–110% for As in both samples while ~60% in the Se in coal fly ash.

However, selenium species could not be extracted quantitatively from sediment samples. Further, the extracts were analyzed for speciation of As and Se using the recommended HPLC–ICPMS procedure. The results are shown in Table 4. In fly ash samples, As(V) and Se(IV) were the predominant species. The difference in concentration of these two elements is mostly dependent upon original concentrations in the coal and combustion conditions during coal burning. The

Table 4
As and Se speciation of microwave extracts of fly ash and sediment

| Sample | As(V) ($\mu g\,l^{-1}$)[a] | As(III) ($\mu g\,l^{-1}$)[a] | $As_{total(ext)}$ ($\mu g\,l^{-1}$)[a] | Se(VI) ($\mu g\,l^{-1}$)[a] | Se(IV) ($\mu g\,g^{-1}$)[a] | $Se_{total(ext)}$ ($\mu g\,l^{-1}$)[a] |
|---|---|---|---|---|---|---|
| Fly ash-1 | | | | | | |
| Water extract | 0.092 ± 0.005 | <0.008 | 0.115 ± 0.003 | 0.22 ± 0.02 | 3.22 ± 0.22 | 3.26 ± 0.18 |
| $H_3PO_4$ extract | 1.70 ± 0.10 | <0.008 | 1.52 ± 0.15 | <0.063 | 3.18 + 0.08 | 3.19 ± 0.19 |
| **Acid digest** | | | **1.49 ± 0.05** | | | **4.79 ± 0.64** |
| Fly ash-2 | | | | | | |
| Water extract | 0.93 ± 0.05 | <0.008 | 0.88 ± 0.04 | <0.063 | 0.53 ± 0.05 | 0.44 ± 0.04 |
| $H_3PO_4$ extract | 10.65 ± 0.10 | <0.008 | 10.19 ± 1.14 | <0.063 | 0.53 ± 0.13 | 0.41 ± 0.03 |
| **Acid digest** | | | **9.2 ± 0.9** | | | **0.95 ± 0.31** |
| Sediment-1 | | | | | | |
| Water extract | 0.20 ± 0.02 | <0.008 | 0.24 ± 0.02 | <0.063 | <0.077 | 0.08 ± 0.02 |
| $H_3PO_4$ extract | 0.57 ± 0.01 | 0.011 ± 0.005 | 0.64 ± 0.09 | <0.063 | <0.077 | 0.07 ± 0.02 |
| **Acid digest** | | | **0.71 ± 0.03** | | | **1.34 ± 0.08** |
| Sediment-2 | | | | | | |
| Water extract | 0.19 ± 0.02 | <0.008 | 0.21 ± 0.04 | <0.063 | <0.077 | 0.08 ± 0.02 |
| $H_3PO_4$ extract | 0.53 ± 0.05 | 0.018 ± 0.005 | 0.60 ± 0.05 | <0.063 | <0.077 | 0.08 ± 0.02 |
| **Acid digest** | | | **0.68 ± 0.05** | | | **1.41 ± 0.28** |

[a] Average of triplicates.

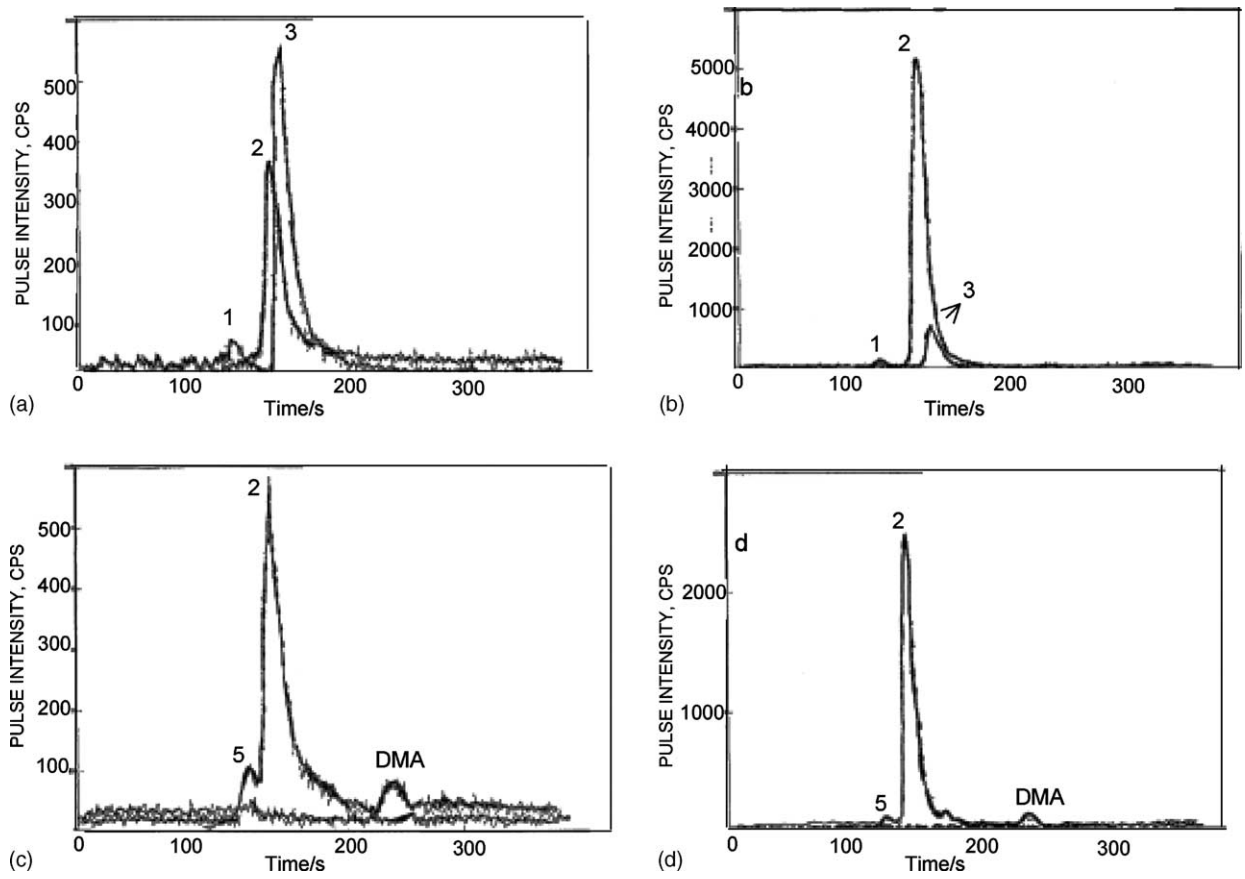


Fig. 3. HPLC–ICPMS chromatogram of coal fly ash and sediment extract (a) coal fly ash (water extract), (b) coal fly ash (1 mM $H_3PO_4$ extract), (c) sediment (water extract) and (d) sediment (1 mM $H_3PO_4$ extract). Peaks are labeled as (1) Se(VI), (2) As(V), (3) Se(IV), (4) As(III) and (5) ArCl.

inter-conversion of species during extraction was not investigated since there were discussed in previous reports [17]. In the sediment samples, only As(V) was mainly found at lower concentrations while Se species were below detection limit. In addition, sediment extracts have shown the presence of DMA at low concentration (0.01–0.02 $\mu g\,l^{-1}$ As). It can be seen from Table 4 data that speciation efficiency for As and Se were better than 95%. Further, spiking experiments in three replicates were carried out for all four species in both fly ash and sediment extracts. The recoveries were in the range of 95–105%. Fig. 3 depicts the chromatogram of fly ash and sediment extracts.

## 4. Conclusion

We have described a rapid separation of inorganic oxyanions of As and Se by HPLC using mixed ion-pairing agents and ICPMS detection. The separation was accomplished in less than 4 min and better detection limits are obtained. The feasibility of the method is demonstrated by analyzing a set of water samples and fly ash and sediment extracts. The results of this experiment indicates the viability of the proposed procedure for speciation of inorganic oxyanions of As and Se in the environmental samples. Because of the close retention time of As(V) and Se(IV), the data processing into Total Chrom work station should be carried out separately though data acquisition was done simultaneously.

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