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# Simultaneous speciation of arsenic, selenium, antimony and tellurium species in waters and soil extracts by capillary electrophoresis and UV detection

The Analyst

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Capillary electrophoresis with indirect UV detection was used to determine simultaneously arsenic, selenium, antimony and tellurium compounds. The separation was achieved in a fused silica capillary filled with an electrolyte solution containing sodium chromate and an electroosmotic flow modifier, trimethyltetradecylammonium hydroxide (TTAOH). The effect of the TTAOH concentration and electrolyte solution pH on the electrophoretic mobility of the species was studied. The best simultaneous separation of these species was achieved with 0.5 mM TTAOH and an electrolyte pH of 11.2 within 5 min. Detection limits range from 13 μg $l^{-1}$ for $Se^{VI}$ to 509 μg $l^{-1}$ for $Te^{IV}$ with electromigrative injection. The reproducibility was below 10% and linearity was verified in the 0–100 mg $l^{-1}$ range for all species. Interferences by other inorganic ions were studied. This method was applied to the determination of metalloids in a spiked drinking water. Water extracts of industrial soils were analysed and results were compared with those of ICP-MS measurements.

## Introduction

The determination of metallic and metalloid species has shown considerable developments in the last 20 years owing to their impact on biological organisms. Metallic and metalloid species closely regulate beneficial and toxicity aspects including human health related issues.[1,2] Increasing attention has recently been paid to As and Se, which occur widely naturally in the environment but also receive significant industrial inputs. The toxicity and ubiquity of As in the environment are generally well established.[3] Selenium is an element which is known to be essential for human health. However, the gap between toxic and essential levels of selenium is narrow and this element is receiving increasing attention.[4] Species of both elements present very different toxicities. Inorganic arsenic forms ($As^{III}$, $As^{V}$) are about 1000 times more toxic than their organic counterparts [monomethylarsonic acid (MMA), dimethylarsinic acid (DMA)].[3] Similarly, inorganic selenium species ($Se^{IV}$, $Se^{VI}$) are more toxic than organic species such as selenocystine (SeCyst).[5]

Although arsenic and selenium have been widely studied, only a few papers have dealt with the determination of tellurium and antimony in the environment. Tellurium compounds are present at picomolar concentrations in sea-water and rainwater.[6] A unique, early study showed that the toxicity of tellurite ($Te^{IV}$) was higher than that of selenite.[7] Karlson and Frankenberger[8] found tellurite to be 10 times more toxic than tellurate ($Te^{VI}$). Trivalent antimony species are more toxic than pentavalent forms.[9] This metalloid has been listed as one of the priority pollutants by the US Environmental Protection Agency.[10]

Previous methods using different separation techniques such as gas chromatography (GC) after derivatization of the analytes to volatile compounds[11–13] and high performance liquid chromatography (HPLC)[14,15] have been commonly used for arsenic and selenium speciation. Capillary electrophoresis has recently been used with success for the determination of arsenic[16–18] and selenium[19,20] species. For tellurium, the separation of inorganic species has been achieved with ion chromatography. Organic compounds were separated by reversed phase HPLC. Both methods were coupled with an ICP-MS detector.[21]

There are only a few examples of the direct separation of antimony compounds. Antimony(III) is most often determined by hydride generation-atomic absorption spectrometry (HG-AAS).[22] The antimony(V) concentration is obtained by the difference between the total antimony and $Sb^{III}$ contents. Smichowski *et al.*[23] recently described methods for the effective separation and determination of inorganic antimony species by HPLC-HG-AAS, HPLC-ICP-MS and HPLC-HG-ICP-MS.

Capillary electrophoresis (CE) was chosen in this study for its high separation potential. It was applied to the simultaneous separation of As, Se, Te and Sb species followed by UV detection. Capillary electrophoresis has higher separation efficiencies than HPLC, GC and ion chromatography. In addition, a wide range of electrolytes are available with this technique, allowing the selection of one that will preserve the integrity of species during the separation process. In this work, the analyses were performed with a chromate-based electrolyte system. This electrolyte is one of the most efficient for indirect UV detection and has recently been used for arsenic[18] and selenium[20] speciation. First the method was optimized; then the applicability to environmental samples (drinking water and soil leachates) was tested in order to evaluate the applicability of the technique to environmental monitoring.

## Experimental

### Instrumentation

This study was performed on a Quanta 4000 capillary electropherograph (Waters Chromatography Division, Millipore, Milford, MA, USA) fitted with a 75 μm id fused silica capillary (Celect, Supelco, Bellefonte, PA, USA) with a total length of 60 cm (52 cm from the inlet to detector window). The analytical voltage was −20 kV. Indirect UV detection was applied at the anodic end of the capillary with a mercury lamp and a 254 nm UV optical filter. In this method, chromate is the chromophore retained to provide the UV absorbance of the electrolyte. Non-absorbing species are detected by the changes occurring in the light absorption due to displacement of the absorbing co-ion.

The capillary was rinsed daily with water for 15 min to prevent the electrolyte from precipitating in the capillary. All analyses were preceded by purging for 2 min with carrier electrolyte to clean the capillary tube. Solutions were injected at the cathodic end of the capillary by hydrostatic or electromigrative injections. For the hydrostatic mode, the sample was injected by raising the carousel 10 cm above its normal position for 30 s. In the electromigrative mode, a high voltage (−10 kV) was applied between the sample and the electrolyte for 20 s prior to the separation step.

### Reagents and species stability

The chromate electrolyte was prepared from sodium chromate ($Na_2CrO_4 \cdot 4H_2O$) (Merck, Darmstadt, Germany) and sodium trimethyltetradecylammonium hydroxide (TTAOH, $C_{17}H_{38}NOH$) was used as an electroosmotic flow modifier. The pH of the solution was adjusted by dropwise addition of 0.3 mol $l^{-1}$ sodium hydroxide solution (Merck). The hydroxy form of the modifier was obtained from sodium trimethyltetradecylammonium bromide ($C_{17}H_{38}NBr$) (Sigma–Aldrich Chimie, Saint-Quentin Fallavier, France) after ion conversion on an ion exchange resin, Amberlite CG 400 (Prolabo, Fontenay sous Bois, France), modified with NaOH. The electrolyte was prepared daily, filtered through 0.45 μm Millipore filters (Millipore, Bedford, MA, USA) and degassed.

Stock standard solutions of 1000 mg $l^{-1}$ arsenic, selenium, antimony and tellurium compounds were prepared from the following commercially available reagents: sodium selenate ($Se^{VI}$) and sodium selenite ($Se^{IV}$) (Merck), DL-selenocystine (SeCyst) and DL-selenomethionine (SeMet) (Sigma–Aldrich Chimie), sodium metaarsenite ($As^{III}$) (Merck), disodium hydrogenarsenate heptahydrate ($As^{V}$) (Prolabo), dimethylarsinic acid (DMA) (Strem Chemicals, Bischheim, France), monomethylarsonic acid (MMA) (Carlo Erba, Nanterre, France), potassium antimonyl tartrate hydrate ($Sb^{III}$) (Sigma–Aldrich Chimie), potassium hexahydroxyantimonate ($Sb^{V}$) (Prolabo), sodium tellurite ($Te^{IV}$) and telluric acid ($Te^{VI}$) (Sigma–Aldrich Chimie). All reagents were used without further purification. Deionized water (18 MΩ $cm^{-1}$ resistance) (Millipore) was used to prepare all reagent and standard solutions.

All standard solutions (1000 mg $l^{-1}$) were stored at 4 °C in the dark. Stability over several months has been observed for arsenic compounds.[24] Selenium standard solutions were stored for a maximum of 1 month at 4 °C in PTFE containers.[25] The stability of the solutions of antimony species was proved to be effective for at least 12 months for $Sb^{III}$ (as potassium antimonyl tartrate hydrate) and $Sb^{V}$ (as potassium hexahydroxyantimonate) in a solution containing the two species.[26] Telluric acid solutions are reported to be stable for several months[6] but no information exists to our knowledge on the stability of $Te^{IV}$. In order to avoid any changes in the speciation of the studied species, fresh working standard solutions were prepared daily by appropriate dilution of the stock standard solutions.

### Soil leachates analytical procedure

No standardized method for the extraction of metalloids from soils is available. The choice of water as the extraction solution is based on the fact that the soil solution is the principal component from which plant roots and microorganisms take up the elements. The water-soluble fraction of metalloids therefore gives an idea of their bioavailability. It seems, therefore, that using water as extractant simulates well natural soil conditions.[27]

In this procedure, 50 ml of de-ionized water were added to 10 g of soil and agitated for 2 h. The solution was filtered through a 0.45 μm Millipore filter and injected into the CE apparatus in the hydrostatic injection mode. A Perkin-Elmer SCIEX (Thornhill, ON, Canada) Elan 6000 inductively coupled plasma mass spectrometer (Perkin-Elmer) was used to validate the CE measurements.

## Results and discussion

Several parameters were carefully studied in order to optimize the simultaneous separation of all species.

### Influence of TTAOH concentration

In the CE separation mode for anions, species are retained owing to the electroosmotic flow taking place towards the cathode. Detection is performed on the anode side. The electroosmotic and electrophoretic movements occur in opposite directions. Alkylammonium salts such as cetyltrimethylammonium bromide (CTAB),[28] tetradecyltrimethylammonium bromide (TTAB)[29] and hexadecyltrimethylammonium bromide (HTAB)[30] and amines such as diethylenetriamine (DETA)[31] have been reported in several applications which require suppression or reversal of the electroosmotic flow. In this work, sodium trimethyltetradecylammonium hydroxide (TTAOH) was used in order to reverse the direction of the electroosmotic flow and to increase the migration velocity of the studied species towards the detector. The hydroxy form of TTAB allowed us to work at high pH values without increasing the ionic strength, which would result in a high background. The effect of TTAOH concentration on the mobility of the compounds in the capillary was studied using the apparent mobility, $\mu_a$, which represents the sum of the electrophoretic and electroosmotic mobilities, calculated using the following equation:

$$\mu_a = Ll/t_m V \quad (1)$$

where $L$ is the total length of the capillary, $l$ the length of the capillary to detector, $t_m$ the migration time of the solute and $V$ the voltage applied during the separation.[32]

The influence of TTAOH concentration was evaluated by injecting all the species of one metalloid simultaneously. The evolution of the individual apparent mobility with the concentration of TTAOH for the 12 species studied is presented in Fig. 1. All curves display the same typical response, which means that TTAOH does not generate selectivity effects. The apparent mobility increases rapidly with increasing TTAOH concentration to reach a plateau at 0.5 mM. These results are in good agreement with those obtained by Gilon and Potin-Gautier[20] and Albert *et al.*[19] for selenium species.

The optimum TTAOH concentration was 0.5 mM, since higher concentrations did not improve the mobility. Furthermore, at high concentrations of the surfactant, the critical micellar concentration is reached and the formation of micelles would alter the separation efficiency. This problem was encountered by Han *et al.*[33] with organotin compounds.

## Influence of electrolyte pH

The pH of the electrolyte is another important parameter in CE. The dissociation constants of the species studied are given in Table 1. This information is essential to determine the ionization capability of the species under different pH conditions. The influence of the electrolyte pH on the apparent mobility of the metalloids was studied in the pH range 8–12 by injecting all the species of one metalloid simultaneously. Acidic pH values were not tested owing to the high p$K_a$ values of species such as $As^{III}$ and $Te^{VI}$. The effective charge of these analytes would not be negative at low pH values. Further, at pH $< 7.5$, precipitation of sodium chromate can occur in the electrolyte.

Fig. 2 displays the evolution of the apparent mobility of the metalloids as a function of the electrolyte pH. The general trend observed indicates that the apparent mobility increases slightly for all the species when the pH is raised from 8 to 11.5. The MMA species is an exception; its mobility appears to be strongly pH dependent.

TTAOH is a neutral quaternary ammonium salt and does not modify the wall of the capillary despite the pH changes. The increase observed in the apparent mobility in the pH range 8–11.5 is therefore probably due to changes in analyte charges. The pH of the electrolyte directly influences the electrophoretic mobility of the analytes. For example, arsenate and selenate possess very low p$K_a$ values and have two negative charges for a wide pH range (Table 1). They will therefore migrate fast compared with arsenite, which has a high p$K_a$ value.

These results are similar to those of Albert *et al.*,[19] who separately studied electrophoretic and electroosmotic mobility of selenium species as a function of pH. They concluded that electroosmotic mobility was not influenced by the pH and that electrophoretic mobility increased with increasing pH.

For MMA, the second p$K_a$ value (8.66) corresponds to the beginning of the pH range investigated. When the pH is around 8, both monovalent and divalent forms of MMA co-exist in equivalent amounts. An increase in pH results in an increased concentration of the divalent form. This results in the inflection observed in the apparent mobility curve [Fig. 2(a)]. These observations are in full agreement with the model developed by McGuffin and Tavares[37] for the prediction of effective electrophoretic mobility (based on acid–base equilibria).

In order to obtain a good compromise between detection and separation of all the species in a short time, a pH of the

**Table 1** The studied species with their p$K_a$ values

| Compound | Formula | p$K_a$ | Ref. |
|---|---|---|---|
| Arsenite ($As^{III}$) | $HAsO_2$ | 9.29 | 34 |
| Arsenate ($As^{V}$) | $H_3AsO_4$ | 2.24<br>6.96<br>11.5 | 34 |
| Monomethylarsonic acid (MMA) | $O{=}As(CH_3)(OH)_2$ | 3.96<br>8.66 | 34 |
| Dimethylarsinic acid (DMA) | $O{=}As(CH_3)_2(OH)$ | 1.78<br>6.14 | 34 |
| Selenite ($Se^{IV}$) | $H_2SeO_3$ | 2.35<br>7.94 | 34 |
| Selenate ($Se^{VI}$) | $H_2SeO_4$ | $<0$<br>1.7 | 34 |
| Selenomethionine | $CH_3{-}Se{-}CH_2{-}CH_2{-}CH(NH_2){-}CO_2H$ | 2.6<br>8.9 | 35 |
| Selenocystine | $(-Se{-}CH_2{-}CH(NH_2){-}CO_2H)_2$ | 2.4<br>8.9 | 35 |
| Antimonite ($Sb^{III}$) | $K_2C_8H_4O_{12}Sb_2$ | | |
| Antimonate ($Sb^{V}$) | $H_6KO_6Sb$ | $<0$ | 36 |
| Tellurite ($Te^{IV}$) | $H_2TeO_3$ | 5.45<br>7.74 | 36 |
| Tellurate ($Te^{VI}$) | $H_2TeO_4$ | 6.17<br>10.38 | 36 |

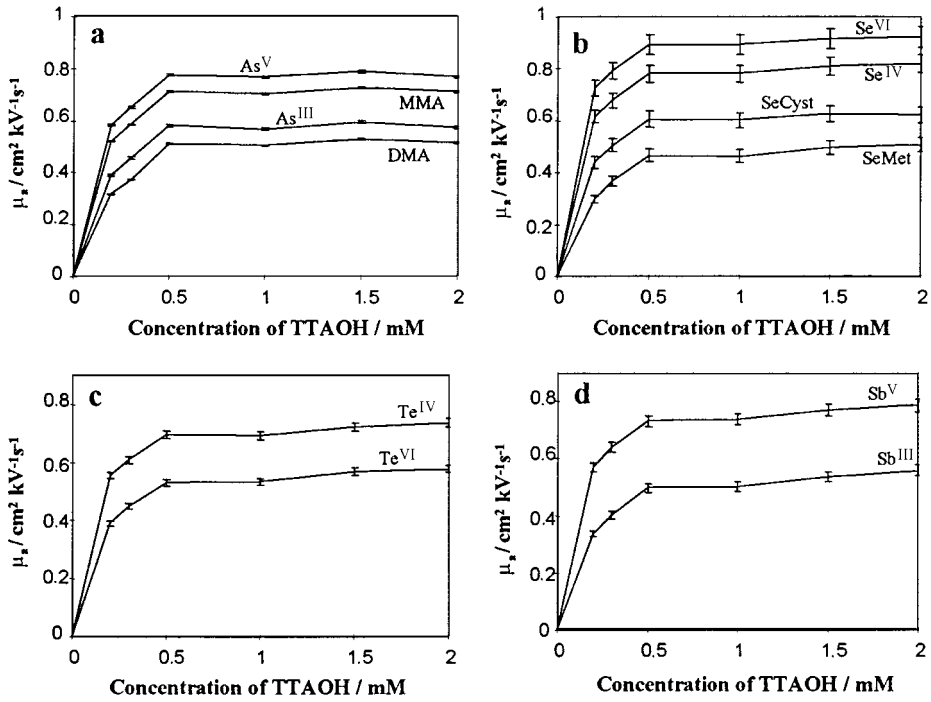


**Fig. 1** Apparent mobility ($\mu_a$) as a function of surfactant (TTAOH) concentration. a, Arsenic compounds; b, selenium compounds; c, tellurium compounds; d, antimony compounds.

electrolyte of 11.2 was adopted. Some species such as SeCyst and SeMet cannot be detected in less than 10 min with pH < 10. For $As^{III}$, $Te^{IV}$ and $Te^{VI}$ species, a pH of the electrolyte > 11 is necessary to allow these species to migrate to the detector. A slow migration velocity of $As^{III}$ was also observed by Schlegel *et al.*[38] and Lin *et al.*[18] at pH 8–9. Further, the $Se^{IV}$ peak cannot be separated from the carbonate peak present on the electropherograms and originating from the carbon dioxide dissolved in the eluent when the pH is < 9.[20]

Careful selection of the pH allows the complete separation of all species simultaneously. Fig. 3 shows the electropherogram of the 12 species studied, which were separated simultaneously. The operating conditions adopted were: sodium chromate 5 mM, TTAOH 0.5 mM and pH of the electrolyte = 11.2. All species were well separated from each other in less than 5 min. Tellurium(IV) shows a poor peak shape, maybe because the electrophoretic mobility of the electrolyte is not closely matched with that of the analyte. A close match is most important, according to Harrold *et al.*,[39] in order to obtain good peak shapes. Interactions between $Te^{IV}$ and the capillary walls may take place and account for the poor peak resolution.

## Analytical figures of merit

The analytical performance of the system was evaluated with two injection modes: hydrostatic and electromigrative injection. The results are presented in Table 2. The reproducibility of the migration time and corrected area (peak area divided by the migration time) was determined for a concentration level of 10 mg $l^{-1}$ for As, Se and Sb and 50 mg $l^{-1}$ for Te with the hydrostatic injection mode. The concentrations used in the electromigrative mode were 1 mg $l^{-1}$ for As, Se and Sb and 5 mg $l^{-1}$ for Te. The data were obtained after six non-consecutive injections. For each injection, a new electrolyte and fresh sample solution containing all the species of one metalloid were prepared in order to assess the reproducibility of the analysis better. The reproducibility was calculated for the simultaneous detection of the species of the same element. A low relative standard deviation (RSD) was obtained, < 7% for the migration time and < 10% for the corrected peak area, with both injection modes.

Detection limits were calculated using the IUPAC definition of $3s/m$, where $s$ is the standard deviation calculated from 10 blank measurements and $m$ is the slope of the calibration graph. The best sensitivities were obtained for most of the species with the electromigrative injection owing to electrokinetic stacking. It remained low owing to the very small sample volumes injected into the capillary (a few nanolitres). The high detection limit observed for $Te^{IV}$ can be related to the fact that $Te^{IV}$ is about four times more UV absorbing than $As^{V}$. The detection limits of selenium species were improved compared with those obtained previously by Gilon and Potin-Gautier.[20] For $Se^{IV}$, the interference generated by the presence of carbonate degraded the detection limit and sensitivity. The detection limits of arsenic species were lower than those obtained by Lin *et al.*[18] using the same chromate buffer. This might be due to the different amount injected or to the UV wavelength used for detection. Conductivity detection gave better detection limits

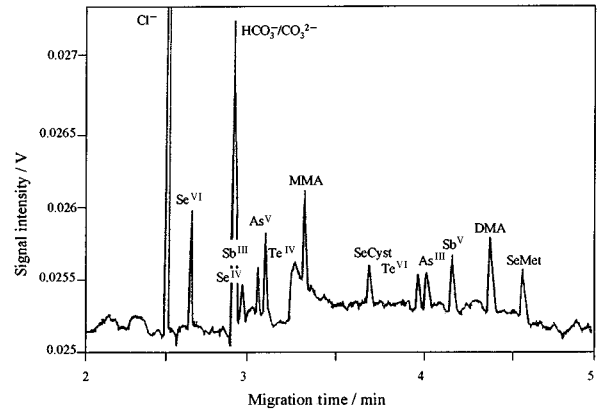


**Fig. 3** Electropherogram of arsenic, selenium, antimony and tellurium compounds. Concentrations: 1 mg $l^{-1}$ for all the species except $Te^{IV}$ (30 mg $l^{-1}$) and $Te^{VI}$ (5 mg $l^{-1}$). Hydrostatic injection (30 s, 10 cm). Separation achieved in 5 min.

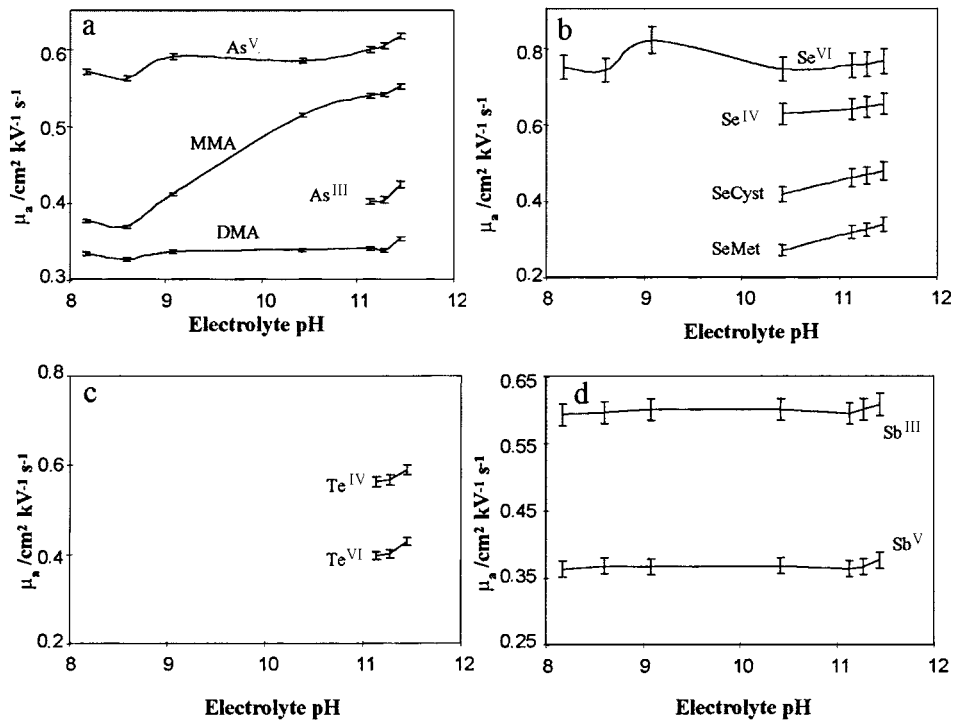


**Fig. 2** Apparent mobility ($\mu_a$) as a function of the pH of the electrolyte. a, Arsenic compounds; b, selenium compounds; c, tellurium compounds; d, antimony compounds.

**Table 2** Analytical figures of merit

| Parameter | Injection mode | $As^{V}$ | MMA | $As^{III}$ | DMA | $Se^{VI}$ | $Se^{IV}$ | SeCyst | SeMet | $Sb^{III}$ | $Sb^{V}$ | $Te^{IV}$ | $Te^{VI}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Migration time/min | | 3.04 | 3.28 | 4.02 | 4.41 | 2.59 | 2.90 | 3.67 | 4.61 | 2.9 | 4.17 | 3.21 | 3.97 |
| Reproducibility of migration time (RSD) (%) | HYD[a] | 0.6 | 0.5 | 1.0 | 0.7 | 4.2 | 4.2 | 4.9 | 5.3 | 2.7 | 3.2 | 2.0 | 2.2 |
| | ELM[b] | 0.8 | 0.7 | 0.6 | 0.8 | 1.2 | 1.1 | 0.9 | 6.8 | 0.6 | 0.6 | 0.2 | 0.6 |
| Reproducibility of corrected area[c] (RSD) (%) | HYD | 4.7 | 5.1 | 6.3 | 5.3 | 3.4 | 9.1 | 4.6 | 6.2 | 9.0 | 2.8 | 7.9 | 5.9 |
| | ELM | 4.4 | 2.5 | 8.5 | 3.9 | 5.2 | 8.6 | 2.3 | 5.2 | 5.5 | 3.8 | 5.3 | 7.7 |
| Detection limit/$\mu g\ l^{-1}$ | HYD | 89 | 84 | 304 | 176 | 52 | 493 | 273 | 106 | 104 | 116 | 3900 | 635 |
| | ELM | 46 | 44 | 124 | 130 | 13 | 124 | 51 | 102 | 64 | 147 | 509 | 346 |
| Linearity (correlation coefficient) | HYD | 0.9992 | 0.9996 | 0.9920 | 0.9990 | 0.9908 | 0.9952 | 0.9995 | 0.9994 | 0.9978 | 0.9987 | 0.9964 | 0.9981 |
| | ELM | 0.9982 | 0.9995 | 0.9911 | 0.9996 | 0.9970 | 0.9951 | 0.9999 | 0.9985 | 0.9996 | 0.9969 | 0.9994 | 0.9961 |
| Linear range/$\mu g\ l^{-1}$ | HYD | $1 \times 10^5$ | $>2 \times 10^5$ | $1.5 \times 10^5$ | $>2 \times 10^5$ | $1.5 \times 10^5$ | $>2 \times 10^5$ | $>2 \times 10^5$ | $1.5 \times 10^5$ | $>2 \times 10^5$ | $>2 \times 10^5$ | $>4 \times 10^5$ | $>4 \times 10^5$ |
| | ELM | $1 \times 10^4$ | $2.5 \times 10^4$ | $2.5 \times 10^4$ | $2.5 \times 10^4$ | $2.5 \times 10^4$ | $0.5 \times 10^4$ | $1 \times 10^4$ | $1 \times 10^4$ | $2.5 \times 10^4$ | $1 \times 10^5$ | $5 \times 10^4$ | $5 \times 10^4$ |

[a] HYD = hydrostatic injection, 30 s, 10 cm. [b] ELM = electromigrative injection, 20 s, −10 kV. Separation conditions: 10 min, −20 kV. UV detection at 254 nm. [c] Corrected area = peak area divided by the migration time.

for arsenic ($As^{III}$, $As^{V}$, DMA) and selenium ($Se^{IV}$) species, except for selenate.[38]

Calibration curves were plotted for both injection modes up to the levels expected in natural samples. Linearity extended up to 400 mg $l^{-1}$, depending on the species investigated, in the hydrostatic injection mode and up to 5–50 mg $l^{-1}$ in the electromigrative injection mode.

### Interferences by other ionic species

Major anions present in the matrix may generate interferences with the species of interest during both separation and detection since UV detection is not a specific method. Therefore, the presence of high concentrations of anions which are always present in natural waters, such as bromide, carbonate, chloride, nitrate and sulfate, could alter the detection stage. The influence of carbonate and nitrate was studied in this particular case because these compounds may co-elute with some of the species of interest.

Increasing concentrations of nitrate and carbonate were added up to 100 mg $l^{-1}$ to a solution containing 2.5 mg $l^{-1}$ of one of the analyte species ($As^{V}$, $Se^{IV}$, $Se^{VI}$ or $Sb^{III}$) in deionized water. Fig. 4 shows the evolution of the resolution factor ($R_s$) with increasing concentration of carbonate and nitrate. The resolution factor is defined as follows:

$$R_s = 2(t_{r_2} - t_{r_1})/(\omega_1 + \omega_2) \quad (2)$$

where $t_{r_1}$ and $t_{r_2}$ represent the retention times of two consecutive compounds and $\omega_1$ and $\omega_2$ the corresponding peak widths. $R_s$ remains above the quantification level ($R_s > 1.5$) only up to 10 mg $l^{-1}$ carbonate for the separation of $As^{V}$–carbonate peaks and $Se^{IV}$–carbonate peaks. Other workers obtained higher limits using different buffer pH conditions.[20] For $Sb^{III}$, the maximum carbonate concentration which still allows $Sb^{III}$ to be determined is 60 mg $l^{-1}$. The interference of nitrate on the selenate peak clearly shows that the resolution factor is always well below the quantification level [Fig. 4(b)]. The occurrence of nitrate in a sample would therefore prevent the quantification of selenate using the analytical conditions optimized in this study.

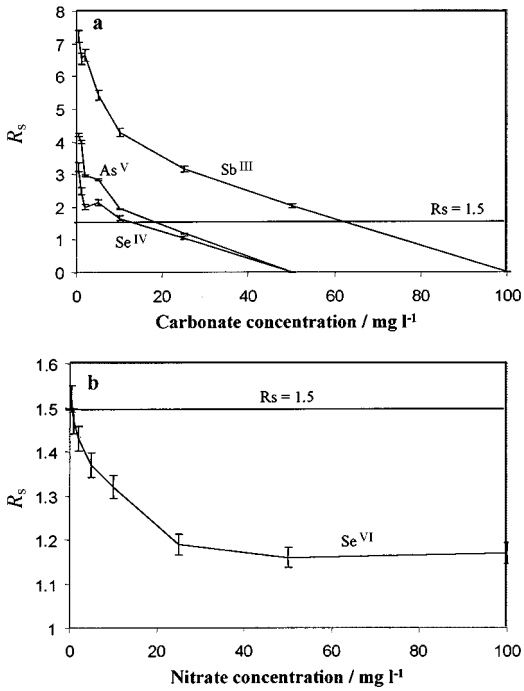


**Fig. 4** Resolution factors between (a) carbonate and $As^{V}$, carbonate and $Se^{IV}$ and carbonate and $Sb^{III}$ and (b) nitrate and $Se^{VI}$.

The other metalloid species are not affected by the presence of nitrate.

### Environmental analysis

**Application to drinking water.** Capillary electrophoresis has been applied previously to the determination of inorganic selenium species in geothermal waters.[40] Difficulties in determining selenium in these matrices were related to the high concentrations of sulfates and carbonates present in the sample. The influence of the major anions on the quantification of the species of interest was evaluated in this study by determining As, Se, Sb and Te in a commercial drinking water (Volvic). This water contains fairly high concentrations of major anions which could interfere with the species studied. A sample of water was spiked with 2 mg $l^{-1}$ of As, Se and Sb species, 60 mg $l^{-1}$ of $Te^{IV}$ and 10 mg $l^{-1}$ $Te^{VI}$. The spiked sample was diluted twofold, to minimize the interferences from the anions present in the matrix. The analyses were performed in the hydrostatic injection mode. The results of the analysis by CE are in good agreement with the concentrations introduced into the sample, the recoveries being 100 ± 5% for $As^{V}$ and MMA, 105 ± 15% for $Sb^{V}$, 101 ± 3% for $Te^{VI}$ and 94–98 ± 5% for $As^{III}$, DMA, SeCyst and SeMet.

The determination of $Se^{IV}$, $Se^{VI}$ and $Sb^{III}$ concentrations was not possible. The carbonate concentration in the sample diluted twofold was 32.7 mg $l^{-1}$, which was too high for the determination of selenite, as shown in Fig. 4(a). The carbonate peak eluted together with $Se^{IV}$. Antimony(III) should have been separated from the carbonate peak according to Fig. 4(a), but a shift of the migration time was observed when the water sample was injected, compared with a standard solution prepared in deionized water. This phenomenon was attributed to the ionic composition of the water sample, which modifies the electrophoretic transport. This was also observed by Lopez-Sanchez *et al.*[17] In spite of a low concentration of nitrate, the $Se^{VI}$ peak co-eluted with nitrate, as expected according to Fig. 4(b). The resolution of the $Te^{IV}$ peak was not sufficient to allow the determination of its concentration.

**Application to soil water extracts.** The method developed in this work was applied to the speciation analysis of the metalloids of interest in water extracts of three industrial soils. These extracts were assumed to contain major anions and also organic matter, which could influence the separation process. In order to assess the effect of the presence of organic matter, an experiment was performed to evaluate the impact of humic substances on the separation of the analyte species. A solution containing 10 mg $l^{-1}$ of As, Se, Sb and Te species and 10 mg $l^{-1}$ of fulvic acids was injected into the CE system. The results showed that migration times of the studied species were unchanged in the presence of fulvic acids. Further, fulvic acids eluted only after 10 min. Organic matter was therefore not expected to interfere with the species of interest in the water extracts.

An electropherogram of one of these water extracts is presented in Fig. 5. Only arsenic species were found to be present in these samples. Inorganic arsenic species were identified and quantified. $As^{V}$ was the main species present, with concentrations ranging from 7.7 to 19.4 mg $l^{-1}$. Arsenic(III) was present at lower concentrations, from 2.5 to 3.5 mg $l^{-1}$. The other metalloids were not present in the samples or were present at concentrations below the detection limits. The arsenic concentrations obtained using CE were in good agreement with the total amount of arsenic evaluated by ICP-MS (Table 3). All the arsenic present in the samples was then assumed to be inorganic arsenic. It was not expected to find methylated arsenic species owing to the low biological activity of these soils and the detection limit of the method.

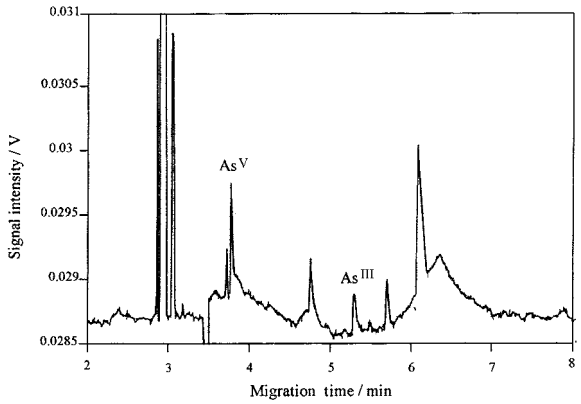


**Fig. 5** Hydrostatic injection of a water extract of an industrial soil. Separation achieved in 10 min at −20 kV.

**Table 3** Arsenic concentrations in water extracts of three industrial soils

| Soil sample | $As^{V}$ concentration/ mg $l^{-1}$ | $As^{III}$ concentration/ mg $l^{-1}$ | Total As/ mg $l^{-1}$ (obtained by CE) | Total As/ mg $l^{-1}$ (obtained by ICP-MS) |
|---|---|---|---|---|
| 1 | 19.4 ± 0.1 | 3.5 ± 0.5 | 22.9 ± 0.6 | 23.4 ± 0.5 |
| 2 | 7.73 ± 0.03 | 3.29 ± 0.06 | 11.00 ± 0.09 | 10.07 ± 0.09 |
| 3 | 15.0 ± 0.2 | 2.5 ± 0.6 | 17.5 ± 0.8 | 19.07 ± 0.09 |

## Conclusion

Capillary electrophoresis is a powerful separation technique and its application to speciation studies has become an important field of investigation. The method developed in this work allowed us to achieve, after optimization of the pH of the electrolyte and the concentration of the electroosmotic flow modifier, the simultaneous separation of 12 organic and inorganic species of arsenic, selenium, antimony and tellurium. The speciation analysis was accomplished within 5 min. The determination of the different species of the four metalloids added to a drinking water and the study of arsenic speciation in water extracts of industrial soils showed that the application of this technique to environmental samples is possible. However, the indirect UV detection method suffers from a lack of sensitivity (detection limits ranging from 13 μg $l^{-1}$ for $Se^{VI}$ to 509 μg $l^{-1}$ for $Te^{IV}$) and specificity. Most of the problems encountered in this study could be solved by the use of a selective and sensitive detection method such as ICP-MS. Our intention is to couple CE with ICP-MS, as described recently.[41–48]

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