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Ion chromatography–hydride generation-atomic fluorescence spectrometry speciation of tellurium

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The speciation of tellurium was carried out using atomic fluorescence spectrometry as an element-specific detector in hybridization with liquid chromatography and hydride generation. Good resolution could be obtained by anion-exchange chromatography with complexing agents, using a mobile phase with 8 mM EDTA and 2 mM potassium hydrogenphthalate. Analysis time was less than 6 min. Calibration graphs were linear between 2 and 100 μg l^{-1}. Detection limits were 0.6 μg l^{-1} and 0.7 μg l^{-1} for tellurium(VI) and tellurium(IV) respectively. The method was applied to the speciation of tellurium in drinking water and wastewater samples from different metallurgical industries. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: tellurium speciation; liquid chromatography; hydride generation-atomic fluorescence spectrometry; water samples

INTRODUCTION

Tellurium is used in the metallurgical industry as an alloy constituent. It is a non-essential element and the species are highly toxic to humans. In aqueous chemistry, tellurium is mainly found as telluride (Te^{2-}), tellurite (TeO_3^{2-}) and tellurate (TeO_4^{2-}).[1] Tellurium(VI) is more abundant, but it is thermodynamically less stable than tellurium(IV). The toxicity of the element depends of its oxidation state, tellurium(IV) being about 10 times more toxic than tellurium(VI). However, very little is known about the speciation of the element. Different separation and preconcentration techniques have been proposed,[2–13] but, because both toxicity and bioavailability depend on the oxidation state, it is very important to develop new speciation methods. The coupling of liquid chromatography (LC) with spectroscopic techniques seemed very promising, and hybridization of LC with inductively coupled plasma atomic mass spectrometry (LC–ICP-MS), as developed by Lindemann *et al.*,[14] allowed multielemental analysis of arsenic, selenium, antimony and tellurium. Atomic fluorescence spectroscopy (AFS) seems to be a simpler alternative, and hybridized LC–HG-AFS offers good analytical characteristics as regards linearity and low detection limits; it is also relatively free of interference and memory effects. The technique is based on the selective determination of tellurium(IV) and it is necessary to reduce tellurium(VI). To the best of our knowledge, no papers concerning the speciation of tellurium by LC–HG-AFS have been published.

This study proposes a new hybridization procedure for the speciation of tellurium(IV) and tellurium(VI) using LC–HG-AFS. Anion-exchange LC with multidentate complexing agents in the mobile phase is used. This is because secondary equilibrium using complexing eluents improves column efficiency for separating metal species. The agents used are EDTA and potassium hydrogenphthalate (KHP), which have a very high complexing capacity and which transform the positive metal ion into negatively charged complexes. The method was applied to the analysis of drinking water and wastewater samples from metallurgical industries.

EXPERIMENTAL

Instrumentation

The LC system consisted of an Agilent 1100 (Agilent, Waldbronn, Germany) liquid chromatograph operating at room temperature with a flow rate of 1 ml min^{-1}. The

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solvents were degassed using an on-line membrane system (Agilent 1100). Aliquots of 400 µl were injected manually using a Model 7125-075 Rheodyne injection valve (Rheodyne, CA, USA). Separation was performed on a Hamilton PRP-X100 (Teknokroma, Barcelona, Spain) strong anion-exchange column (150 mm × 4.1 mm, 10 µm).

HG-AFS was performed using a PSA Millenium Excalibur continuous-flow system (PS Analytical, Orpington, UK) with a PSA 10 570 UV cracker. Measurements were carried out using a boosted discharge hollow cathode lamp for tellurium (Photron Pty Ltd, Australia) at the 214.3 nm line, with a 15 mA primary current and a 17.6 mA boost current. The conditions for HG-AFS were: flow rates at 5 ml min^{-1} for the 5 M hydrochloric acid and at 2.5 ml min^{-1} for the 2% (m/v) sodium tetrahydroborate solutions. The U-shaped gas–liquid separator was flushed with argon gas and the volatile hydride produced was swept by the stream of argon (270 ml min^{-1}), passed through a Perma Pure hygroscopic membrane (Farmingdale, NJ, USA) and atomized using a hydrogen diffusion flame. Valves and T-pieces were obtained from Omnifit (Cambridge, UK). An EBA 20 centrifuge (Hettich, Germany) was also used.

Mineralization of the samples for comparison purposes was carried out on a P-Selecta hot plate. Total tellurium quantification was carried out by AFS with the PSA Millenium Excalibur.

Reagents and samples

All the solutions were prepared with deionized water (18 MΩcm) purified through a Millipore purification system (Millipore, Bedford, MA, USA). The glassware was thoroughly acid washed with a 10% v/v nitric acid solution and rinsed with deionized water prior to use.

Stock solutions of 1000 µg ml^{-1} were prepared by dissolving sodium tellurite and sodium tellurate (Aldrich, Milwaukee, USA) from the commercial products using 0.5% (v/v) nitric acid. The tellurite standard contained a small amount of tellurate, and a 100 µg ml^{-1} solution was prepared by heating an aliquot with 5 ml of concentrated hydrochloric acid at 80 °C for 30 min to achieve its total reduction. This solution was stable at 4 °C for several months. The complexes of tellurium with citric acid were prepared by mixing 1 ml of tellurium standards with 9 ml of 50 mM citric acid and maintaining at room temperature for 15 min. Diluted solutions were prepared daily with 50 mM citric acid.

The mobile phase was an 8 mM EDTA–2 mM KHP (Aldrich) solution daily prepared. The 2% (m/v) sodium tetrahydroborate solution was prepared daily by dissolving sodium tetrahydroborate (Aldrich) in 1% (m/v) sodium hydroxide solution and the 5 M hydrochloric acid solution was diluted from the concentrated acid (Fluka). Nitric acid (65% m/v, Aristar, Poole, Dorset, UK), citric acid and potassium iodide (Fluka), and sodium hydroxide pellets were also used.

The water samples were five samples collected from different purification plants and eight wastewater samples obtained from different metallurgical industries.

Procedures

Aliquots of water samples were centrifuged at 6000 rpm for 5 min, filtered through 0.45 µm nylon Millipore chromatographic filters and injected into the chromatograph to carry out the tellurium speciation.

To confirm the reliability of the procedure, the samples were previously analysed for comparison purposes. An aliquot of 5 ml of water was treated with 5 ml of concentrated hydrochloric acid and the solution was heated at 80 °C for 30 min to reduce tellurium(VI) to tellurium(IV). After this treatment, the samples were cooled before dilution with deionized water in 10 ml volumetric flasks. Aliquots were analysed by HG-AFS.

RESULTS AND DISCUSSION

Optimal conditions for the HG-AFS hybridization

Tellurium(IV) is the only tellurium species that generates the hydride, and several reducing agents were assayed to reduce the tellurium(VI). Figure 1 shows the influence of the different reagents on the fluorescence of a 50 ng ml^{-1} tellurium(VI) solution directly aspirated to the AFS. As can be seen, the best results were obtained using potassium iodide, which was selected for further experiments.

To improve the reduction efficiency of tellurium(VI), the effect of temperature was studied by introducing a 5 m coil reactor in a thermostated bath. Figure 2 shows that the signal increased strongly for tellurium(VI) up to 100 °C, whereas for tellurium(IV) it decreased slightly above 60 °C. This effect could have been caused by the chlorine-originated oxidation of tellurium(IV). The use of a UV cracker to reduce tellurium(VI) was also assayed, but lower fluorescence signals were obtained for both species with the cracker.

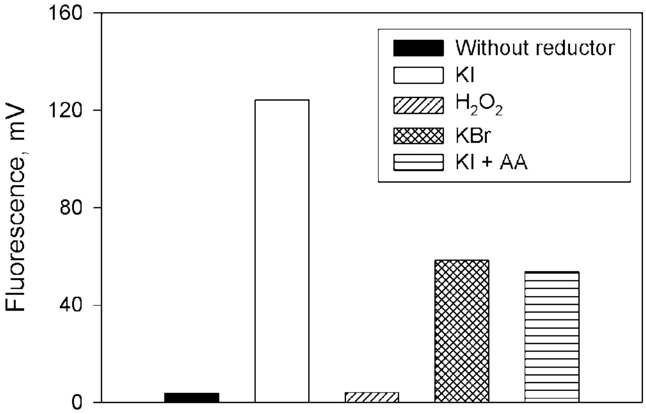

Figure 1. Effect of several reducing agents on the AFS signal of a 50 µg l^{-1} tellurium(VI) solution. Concentrations were 1.5% (m/v) potassium iodide, 2% (m/v) hydrogen peroxide, 2% (m/v) potassium bromide and 1.5% (m/v) potassium iodide, plus 1% (m/v) ascorbic acid.

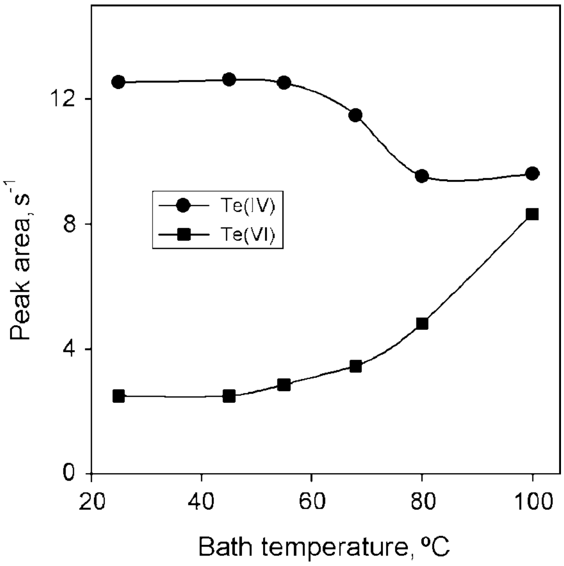

Figure 2. Influence of the coil reactor temperature on the signals of tellurium(IV) and tellurium(VI) (100 μg l^{-1} each). Reagent concentrations: 1.2% (m/v) sodium tetrahydroborate, 4 M hydrochloric acid, 1.5% (m/v) potassium iodide. Argon flow, 270 ml min^{-1}.

Consequently, a temperature of 100 °C was selected, thus producing similar signals for both tellurium species.

When the variation of the fluorescence with the hydrochloric acid concentration was studied in the 1–9 M range, the fluorescence increased rapidly with increasing acid concentrations up to 5.5 M, and then decreased strongly (Fig. 3a). Thus, a 5 M concentration was chosen, which also provided the maximum signal-to-background ratio for both species. The sodium tetrahydroborate concentration was varied between 1 and 3% (m/v) (Fig. 3b); since the maximum sensitivity was achieved with a 2% (m/v) concentration, this was selected because higher percentages led to higher noise. When the concentration of potassium iodide was varied in the 0–3% (m/v) range, fluorescence increased up to 1.5% (m/v), remaining constant for higher concentrations (Fig. 3c); thus, a 2% (m/v) value was chosen. The flow rate for the hydrochloric acid solution containing potassium iodide was varied between 2 and 8 ml min^{-1}, and a value of 5 ml min^{-1}, which provided the maximum peak area and an appropriate flame stability, was selected. For the sodium tetrahydroborate channel, flow rate was varied between 1.5 and 3 ml min^{-1}, and a value of 2.5 ml min^{-1} was selected (which gave maximum sensitivity), since higher values led to high noise signals.

Optimization of the liquid chromatographic separation

The two inorganic tellurium species eluted at the void time when using the anion-exchange column and could only be separated by means of a secondary equilibrium using complexing eluents, such as EDTA and KHP. However, even in the presence of these complexing agents, tellurium species were not retained in the column, and so a new approach based on the formation of the citric acid complexes was tried. This procedure was previously reported for the separation of antimony species.[15] Thus, the citric acid complexes of both inorganic tellurium species were formed as indicated in the Experimental section and submitted to the chromatographic procedure. The influence of the complexing reagent concentrations was then studied. The presence of EDTA in the mobile phase in the 0–16 mM range decreased the retention time of tellurium(IV) strongly, especially at higher EDTA concentrations (Fig. 4a); tellurium(VI), however, was not affected, as it eluted at the solvent front.

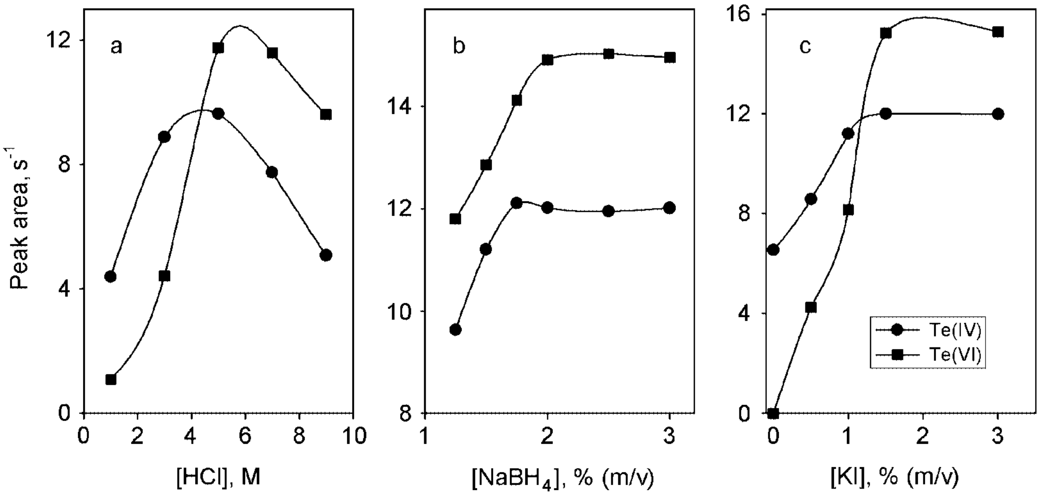

Figure 3. Influence of the hydrochloric acid (a), sodium tetrahydroborate (b) and potassium iodide (c) concentrations on the signals of tellurium(IV) and tellurium(VI) (100 μg l^{-1} each). Reagent flows:, sodium tetrahydroborate, 2.5 ml min^{-1}; hydrochloric acid and potassium iodide, 4 ml min^{-1}. Temperature, 100 °C. Argon flow, 270 ml min^{-1}.

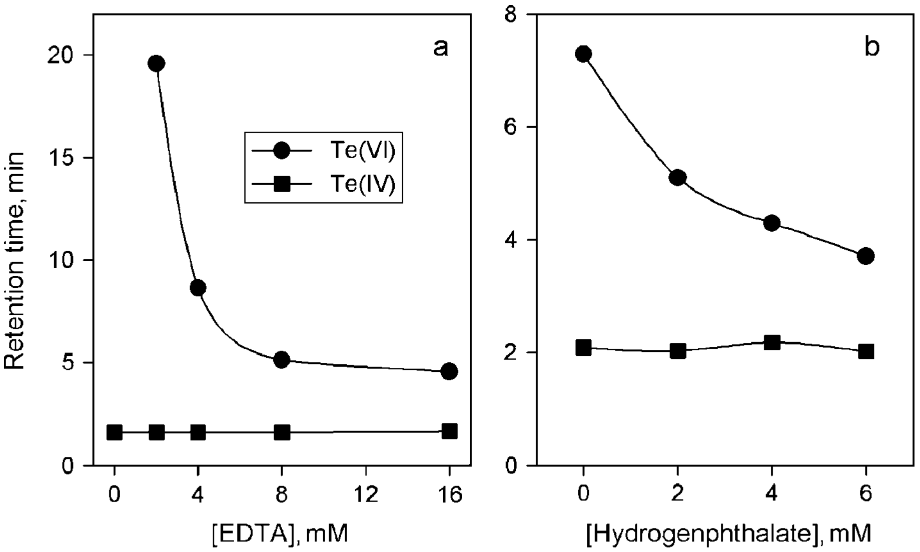

Figure 4. Influence of the mobile phase composition on the chromatographic retention of tellurium species. (a) Effect of EDTA concentration; (b) effect of KHP concentration. Flow rate, 1 ml min^{-1}.

An 8 mM EDTA concentration allowed good separation of tellurium(IV) and tellurium(VI). The addition of another competing ligand, KHP, to the mobile phase was assayed at 0–6 mM. This anion did not modify the behaviour of tellurium(VI), but produced a substantial reduction in both the retention and the peak width of tellurium(IV); a 2 mM concentration was selected, since this gave sharper peaks (Fig. 4b). The effect of the citric acid concentration on complex formation was also studied. The concentration of this chemical was varied in the 0–80 mM range and complexes were formed as indicated in the Experimental section. When the complexes were injected, the retention for tellurium(IV) increased up to a 50 mM concentration and then remained constant, whereas the retention of tellurium(VI) was not affected by the concentration of the complexing agent. Thus, a 50 mM citric acid concentration was selected. Figure 5 shows the profile obtained in the chromatographic conditions selected. Retention times were 2.4 min and 5.6 min for tellurium(VI) and tellurium(IV) respectively.

Calibration, repeatability and detection limits

Calibration graphs were made by plotting peak area against concentration (micrograms of tellurium per litre), using linear regression analysis. Table 1 shows the equations obtained for the calibration graphs and the regression coefficients. The detection limits were calculated on the basis of 3σ (σ being the residual standard deviation around the regression line), using the regression lines for the standards. The precision of the method was demonstrated by repeated analyses, calculating the average relative standard deviation (RSD) for 10 replicate injections of the same sample at the 20 μg l^{-1} concentration level. Values are given in Table 1.

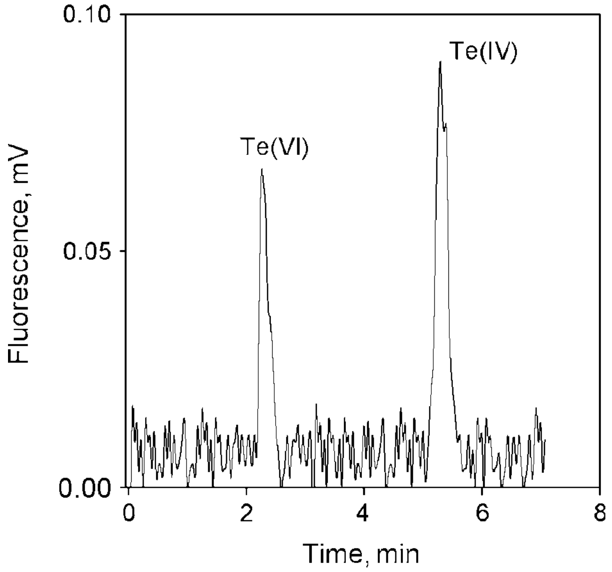

Figure 5. Elution profile obtained for tellurium(VI) and tellurium(IV) using a mobile phase containing 8 mM EDTA and 2 mM KHP (pH 4.4). Flow rate, 1 ml min^{-1}. Standard concentrations, 5 μg l^{-1}.

Recovery studies and environmental applications

The proposed method was evaluated by analysing tellurium species in spiked water samples, because there are no certified reference materials. A recovery study was carried out by spiking the samples with both tellurium species at the 20 μg l^{-1} level. No sample matrix interferences were found, because the slopes of standard additions were similar to those of the aqueous calibration graphs

Table 1. Analytical characteristics of calibration graphs

	Te(VI)	Te(IV)
Intercept	−1.941	−2.004
Slope	0.741	0.713
Correlation coefficient	0.9999	0.9999
Te linearity range (μg l^{-1})	2–100	2–100
Te detection limit (μg l^{-1})	0.69	0.76
RSD (%)	4.1	4.0

Table 2. Recovery studies in spiked water samples

	Recovery, mean ± SD (%)	
Sample	Te(VI)	Te(IV)
Drinking water 1	95.8 ± 3.8	96.0 ± 2.8
Drinking water 2	98.6 ± 4.3	96.5 ± 4.4
Drinking water 3	97.6 ± 3.6	99.0 ± 4.8
Drinking water 4	96.0 ± 3.0	97.3 ± 3.9
Drinking water 5	98.6 ± 3.5	96.9 ± 4.9
Wastewater 1	98.5 ± 2.4	97.2 ± 1.4
Wastewater 2	97.5 ± 3.0	95.8 ± 2.6
Wastewater 3	95.7 ± 2.1	96.2 ± 3.3
Wastewater 4	96.7 ± 3.4	98.1 ± 2.6
Wastewater 5	95.6 ± 2.1	97.9 ± 3.5

Table 3. Speciation of tellurium in waste water samples[a]

	Te speciation (μg l^{-1})		Total Te (HG-AFS)
Sample	Te(VI)	Te(IV)	(μg l^{-1})
Wastewater 1	7.5 ± 0.2	ND	7.0 ± 0.1
Wastewater 2	6.5 ± 0.2	ND	6.1 ± 0.3
Wastewater 3	2881 ± 48	ND	2784 ± 73

[a] ND: not detected.

and the recoveries were practically quantitative in both drinking water and wastewater samples (Table 2). Then, the samples were treated as indicated in the experimental procedure and were injected into the chromatograph using the HG-AFS detector. Five water samples from different purification plants were analysed and no tellurium was found above the detection limits, thus confirming the purity of the drinking water. However, in three wastewater samples obtained from metallurgical industries, tellurium was found at levels ranging from 6 to 2881 μg l^{-1}. Table 3 shows the speciation analysis using the LC–HG-AFS procedure and the total tellurium content measured by HG-AFS in the wastewater samples. The only species found was tellurium(VI); no tellurium(IV) was identified in any of the samples, above the detection limit. A good concordance appeared; consequently, there are no significant differences between the results obtained by either method.

CONCLUSIONS

The hybridized LC–HG-AFS method provided good linearity and low detection limits for the speciation of tellurium. Anion-exchange chromatography with complexing agents in the mobile phase can be used for the separation of tellurium(VI) and tellurium(IV). The procedure was applied to the speciation of tellurium in wastewater samples from metallurgical industries with excellent results. The method is simpler than other hybridized atomic systems and offers an appropriate alternative to LC–HG-ICP–MS, allowing speciation of tellurium with low detection limits.

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