

Analytical note

Determination of tellurium at ultra-trace levels in drinking water by on-line solid phase extraction coupled to graphite furnace atomic absorption spectrometer

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Received 14 August 2007; accepted 12 November 2007

Available online 21 November 2007

Abstract

In this paper, two time-based flow injection (FI) separation pre-concentration systems coupled to graphite furnace atomic absorption spectrometry (GFAAS) for tellurium determination are studied and compared. The first alternative involves the pre-concentration of the analyte onto Dowex 1X8 employed as packaging material of a micro-column inserted in the flow system. The second set-up is based on the co-precipitation of tellurium with La(OH)₃ followed by retention onto XAD resins. Both systems are compared in terms of limit of detection, linear range, RSD%, sample throughput, micro-columns lifetime and aptitude for fully automatic operation.

The features of the Dowex system are: 37% efficiency of retention and an enhancement factor of 42 for a pre-concentration time of 180 seconds (sample flow rate=3 ml min⁻¹) with acetic acid elution volumes of 80 μl. The detection limit (3 s) is 7 ng l⁻¹ and the relative standard deviation ($n=7200$ ng l⁻¹) is 5.8%. The analytical performance of the XAD system is: 72% efficiency of retention and an enhancement factor of 25 for a pre-concentration time of 180 s (sample flow rate=3 ml min⁻¹) with nitric acid elution volumes of 300 μl. The detection limit is 66 ng l⁻¹ and the relative standard deviation ($n=7200$ ng l⁻¹) is 8.3%.

Applications to the determination of tellurium in tap water and the validation of the analytical methodology employing SRM 1643e as certified reference material are shown.

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Keywords: Flow injection; Electrothermal atomic absorption spectrometry; On-line solid phase extraction; Tellurium determination

1. Introduction

Tellurium is a rare element in the Earth's crust but its use in many technological processes results in local enrichment and release [1]. The emission of inorganic tellurium compounds in the environment may create serious problems owing to the toxicity of this element. In addition and after microbial action, it can be transformed into volatile organometalloid compounds

with the consequent modification of its transport pattern and toxicological behavior [2].

Since the concentration of total tellurium in natural waters is far below the μg l⁻¹ level, very sensitive methods or pre-concentration procedures are necessary for its determination.

Muangnoicharen et. al [3] described a procedure for the determination of inorganic forms of tellurium in air that combines a previous separation using anionic and cationic resins with analysis by graphite furnace atomic absorption spectrometry.

A method based on multicommutated flow system has been developed by Miguel de la Guardia et al. [4] for hydride

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generation, atomic fluorescence (HG-AFS) determination of Te (IV) and Te(VI) in milk samples.

Flow injection (FI) coupled to high performance detectors, i.e. electro-thermal atomizers, appears as a powerful tool for on-line separation, pre-concentration and determination of micro-amounts of metals and metalloids. The possibility of fully automation and the elimination of the usual drawbacks of the off-line work at the sub-ppb level encourage the employment of these hyphenated techniques. Several FI-systems involving different strategies have been described in the literature [5–7]. Among these strategies, the solid phase extraction in packed micro-columns [8–11] and the precipitation or co-precipitation of the analyte followed by its collection on adsorbent resins [12–15] or knotted reactors [16–20] are the most popular.

These approaches require a careful optimization of the variables affecting the performance of the analytical methodology such as: the design of the flow injection manifold including the geometry and location of the micro-column, the characteristics of the filling, the eluant and the volume of elution, the sample flow rate, the pH of retention and elution, the heating program in the graphite furnace atomizer, the matrix modification and the coupling between the flow system and the atomizer.

In this work, two FI-GFAAS systems for the determination of tellurium in tap water are studied and compared. The first approach is based on the on-line pre-concentration of the analyte onto a strong anionic resin (Dowex X8) employed as packaging material of a micro-column inserted in the flow system. The second approach is based on the co-precipitation of tellurium with $\text{La}(\text{OH})_3$ followed by retention onto adsorbent fillings (XAD resins). Regarding the conditions for optimization of the graphite furnace operation, those found by the authors in a previous paper [21] were employed throughout this work.

Both optimized systems will be compared in terms of limit of detection, linear range, RSD%, sample throughput, micro-columns lifetime, easiness of operation, aptitude for a successful coupling flow system-discrete analyzer, etc.

The applications to the determination of tellurium in tap water will be shown as well as the validation of the analytical methodology employing SRM 1643e as certified reference material.

2. Experimental

2.1. Reagents

All reagents were analytical reagent grade. Doubly deionized water (DIW, 18 Mohm-cm) obtained from a Milli-Q water System (Millipore, Bedford, MA, USA) was used throughout the experiments. All operations were performed on a laminar flow clean bench. All laboratory ware was thoroughly cleaned with (1+1) nitric acid and rinsed with DIW.

Te(IV) and Te (VI) stock standard solutions (0.1 g l^{-1}) in nitric acid were prepared by dissolving sodium tellurite (BDH) and sodium tellurate dihydrate (Aldrich) in HNO_3 5% (v/v) (Merck), respectively. Working standard tellurium solutions ($50\text{--}400 \text{ ng l}^{-1}$) were prepared by appropriate dilution of stock standard solutions. Dilutions were performed in calibrate Nalgene flasks (Nalge, Rochester, NY).

Table 1

Graphite furnace temperature program for the determination of tellurium using iridium as a permanent modifier

Step	Temp./°C	Ramp time/s	Hold time/s	Ar flow/mL min^{-1}
Drying	80	30	10	0
Drying	120	30	10	250
Pyrolysis	1000	20	10	250
Pyrolysis	1000	–	30	250
Pyrolysis	1000	–	5	0
Atomisation	2500	–	5	0

Strongly basic anion exchanger Dowex 1X8 (100–200 mesh, Bio-Rad Laboratories, Richmond, CA) and Amberlite XAD-4 resin (20–50 mesh, Rohm and Haas, Philadelphia, PA, USA) were used. The exchanger was conditioned with 0.1 M HCl and thoroughly washed with DIW and then, it was employed for the retention/pre-concentration of the analyte. Acetic acid 1 M solution prepared by dilution of glacial acetic acid was used for elution.

The surface of Amberlite resin was activated by immersion in 4 M HCl/methanol solution (1:1) and washed with DIW and buffer solution. In order to reach the desired pH values, the buffer solutions were prepared by adding different amounts of 0.2 M ammonia to a 0.2 M solution of ammonium chloride. The lanthanum nitrate solution (0.5% m/v) was prepared by dissolving 0.66 g of lanthanum nitrate hexahydrate in 100 mL of DIW. Nitric acid solution 5% (v/v, Merck, Darmstadt, Germany) was employed for elution. Ir solutions (1 g l^{-1} , SPEX plasma standard containing 10% (v/v) HCl) were used as permanent matrix modifiers.

Water standard reference material SRM 1643e from National Institute of Standards and Technology (NIST) was employed to test the methodology proposed.

2.2. Instrumentation

A Shimadzu 6700 Atomic Absorption Spectrometer (Kyoto, Japan) equipped with a graphite furnace accessory GFA 6000 and an autosampler ASC-6000 was used. A Hamamatsu hollow cathode lamp was employed as radiation source at 214.3 nm with a slit width of 2 nm and 8 mA lamp current. The measurements were performed in peak height and integrated area absorbance mode. Background correction was performed using a deuterium lamp. Standard pyrolytic graphite tubes (Shimadzu) were used. The furnace temperature program for the tellurium determination using iridium as a permanent modifier, is given in Table 1. High purity argon was used as the internal gas (AGA, Argentina). Note that the argon flow was cut off during drying in order to improve the precision which could be impoverished due to the large injection volumes employed throughout the experiments.

2.3. Pre-concentration systems

2.3.1. Dowex 1X8

The pre-concentration system is shown in Fig. 1. The micro-column (C) was constructed from an acrylic cylinder (3.0 cm

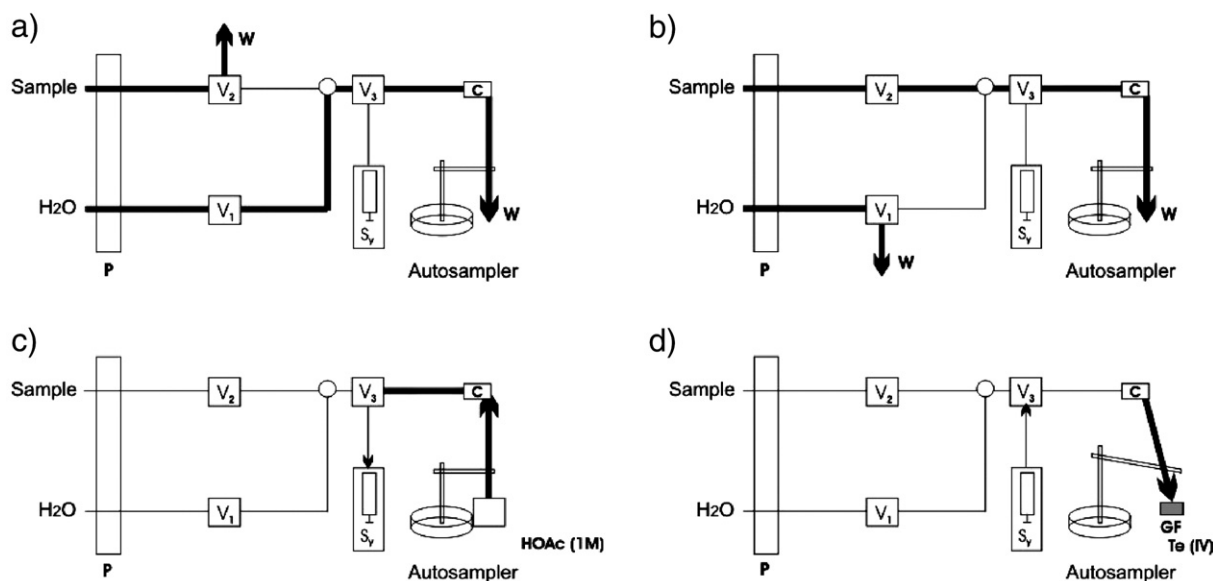


Fig. 1. Flow injection manifold and sequence of operations for the separation pre-concentration system. Thick lines show flows at different stages. (a) washing column, (b) sample loading, (c–d) elution; P, peristaltic bomb; V1, valve 1; V2, valve 2; V3, valve 3; Sy, autosampler syringe; C, microcolumn loaded with the strongly basic anion exchanger; W, waste; GF, graphite furnace.

long, 1.6 cm diameter) furnished with 0.25–28 female connectors. The inner part was drilled to obtain a 28 μl bed volume (15 mm long, 1.5 mm id). The micro-column was slurry loaded with the resin by means of a syringe and then, it was used for at least 50 enrichment cycles before re-packing. Two plugs of polystyrene foam were placed at both sides of the filling in order to retain the resin. The FI manifold was assembled with zero

dead volume using Cheminert fittings (Valco Instruments, Houston, TX) and PTFE tubing (0.5 mm id). An Ismatec MS Reglo (Ismatec, Glattburg, Germany) four channels, six rollers peristaltic pump was used. The pump was controlled via the analogue external port. Tygon tubes were used for pumping all the solutions. Three-way solenoid valves (Cole Parmer, IL) were employed to switch streams. V1 and V2 were PEEK zero dead volume solenoid valves (one inlet, two outlets); V3 was a PTFE manifold valve with two inlets and one outlet. An eight independent relays circuit controlled through the serial port of the computer switched the valves and pump. Interfacing of the FI system to the graphite furnace was achieved by simply connecting one inlet of V3 to the autosampler syringe and the V3 outlet to the sample introduction capillary of the autosampler arm.

2.3.2. XAD-4

The pre-concentration system is shown in Fig. 2-a. An optimization process was carried out using Box–Behnken experimental design [22] involving the variables: pH, sampling flow-rate and lanthanum nitrate concentration with absorbance as analytical response. The experimental data were processed using the STATISTICAL program.

Table 2
FI separation pre-concentration program sequence for Dowex 1X8

Stage	Operation	Fig. 1	Time (s)	Sample flow rate (mL min^{-1})
1	Column washing	Part (a)	30	0
2	Sample loading	Part (b)	180	3
3	Sucking 1 M HAc	Part (c)	5	0
4	Injection	Part (d)	40	0

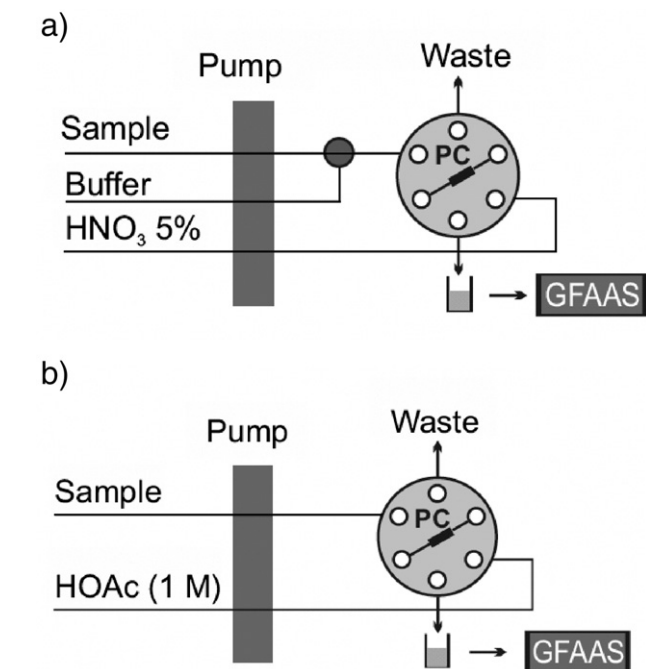


Fig. 2. Flow injection manifolds for the optimization of the pre-concentration process: a) XAD resin; b) Dowex 1X8 resin.

2.4. Procedure

2.4.1. Dowex 1X8

The graphite tubes were pre-treated with the iridium modifier as indicated in a previous paper [23]. The operation sequence of the FI manifold is shown in Fig. 1. Water flow rates, sample flow rates and time intervals for each stage are shown in Table 2. Pre-washing is performed in step (a) to rinse the manifold tubing and the micro-column with water. Step (b) is the sample-loading step. In steps (c) and (d) the species sorbed onto (C) are eluted with 1 M HAc into the graphite furnace: V3 is switched to connect the pre-concentration column to the GFAAS autosampler syringe as in the normal analysis mode. The peristaltic pump is stopped and the autosampler arm starts its operation by aspirating the eluants into the sample injection capillary. Since the micro-column is inserted in the robotic arm of the autosampler as close as possible to the injection tip (see Fig. 1), the eluant can easily reach the filling. The eluant is aspirated in the opposite direction to that of pre-concentration, thus maximizing the contact between eluant and resin, which is performed twice. Moreover, errors derived from incomplete elution due to compaction of the filling are minimized. The autosampler programme also includes air segmentation to prevent dispersion and/or mixing between solutions.

2.4.2. XAD

Standard solutions of tellurium and water samples (flow-rate 3.0 ml min^{-1}) were mixed on-line with the buffer solution. This mixture was loaded on the micro-column for 180 s with the valve V in the loading position (Fig. 2-a). Afterwards the peristaltic pump was stopped, the injection valve was switched to the inject position and the retained analyte was eluted with 5% v/v nitric acid solution. The eluate was collected in plastic vials for their posterior measurement in the graphite furnace.

3. Results and discussion

3.1. Optimization of the FI pre-concentration and separation procedure

Two different approaches were considered for the pre-concentration step: in the first one the sample was pumped

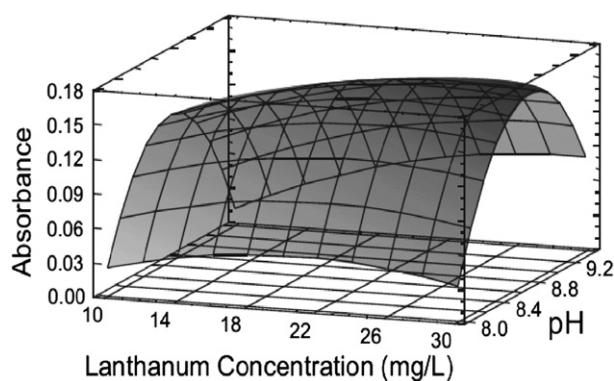


Fig. 3. Three-dimensional plot for the response of the analyte as a function of pH and lanthanum concentration.

Table 3
Main characteristics of both FI procedures

Parameter	Dowex 1X8 ^a	Amberlite XAD-4 ^b
Sample volume (ml)	9	9
Pre-concentration time (s)	180	180
Enhancement factor ^c	42 +/- 2	25 +/- 2
Efficiency (%) ^d	37	72
Elution volume (μl)	80	300

^a On-line operation.

^b Off-line operation.

^c Calculated as the ratio between the analyte concentration that produces an absorbance value for the direct injection of sample equal to that of a solution pre-concentrated and eluted under the described conditions.

^d Compared with the total mass of analyte loaded onto the column.

through the micro-column packed with a strongly basic anion exchanger Dowex 1X8; in the second approach the sample was mixed with a solution of lanthanum nitrate and buffer followed by retention onto the adsorbent resin Amberlite XAD-4 (both manifolds are shown in Fig. 2).

A time-based system instead of a volume based one was preferred for samples loading. The time-based alternative is more flexible as the amount of analyte loaded onto the micro-column can be changed by simply changing the loading time.

Since the characteristics of the filling material, the micro-column dimensions and the volume and kind of eluant seriously influence the performance of the pre-concentration step and the recovery of tellurium, special care was taken to find the best working conditions.

In order to optimize the pre-concentration step and to adequate the elution volumes to the graphite furnace needs, the micro-column was designed to keep minimal dispersion of the sample and the eluant, being the optimal aspect ratio (length to diameter) of the inner beds 15 mm long and 1.5 mm id. Internal diameters smaller than 1.5 mm were not used since leaks in the system were observed because of the developed internal pressures. As the FI manifold has a time-based control, the influence of the contact time sample/filling on the retention of the analyte was investigated. The flow rates and pre-concentration times were varied in order to keep constant the total mass of analyte loaded onto the column. No significant differences were observed in the concentration efficiency for sample flow rates ranging between 1 and 5 ml min^{-1} . However, a flow rate of 3 ml min^{-1} was chosen, as higher values should lead to a poor reproducibility in the long-term operation due to progressive

Table 4
Figures of merit for the FI-GFAAS determination of Tellurium

Parameter	Dowex 1X8 ^a	Amberlite XAD-4 ^b
Detection limit, (ng l^{-1}) ^c	7	66
Linear dynamic range (ng l^{-1})	23–400	220–1000
Precision, RSD, $n=7$, 200 ng l^{-1} and 500 ng l^{-1} (%)	5.8	8.3
Sampling frequency (sample h^{-1})	10	8

^a On-line operation.

^b Off-line operation.

^c Calculated on the basis of three times the standard deviation for 10 replicate measurements of the blank.

Table 5
Determination of Te in NIST 1643e water standard reference material

Element	Certified/ $\mu\text{g l}^{-1}$ (95% confidence)	Found/ $\mu\text{g l}^{-1}$ ($n=5$; 95% confidence) ^a
Te	1.09 \pm 0.11	1.04 \pm 0.11

^a Using Amberlite XAD-4 as preconcentration system.

compaction of the resin. Lower values unnecessary enlarge the pre-concentration times and thus, the sample throughput.

On the belief that Dowex X8 should be useful for the direct determination of inorganic species of tellurium, preliminary experiments were dedicated to use this system for the quantification of tellurite and tellurate. However, it was not possible to find experimental conditions to perform a successfully discrimination between both chemical forms. So, further experiments were dedicated to the determination of total tellurium.

Since tellurite and tellurate are predominant at pH values above 9, experiments for optimizing the retention efficiency of the resin were carried out at pH values ranging between 9.3 and 11.5. The best results were obtained in the range 10.3–10.8.

Acetic acid (0.1–3 M) and nitric acid (0.1–1 M) were assayed for the elution of preconcentrated tellurium. Acetic acid 1 M was selected instead of nitric acid as no long-term operation was possible with the latter due to the rapid deterioration of the resin.

Regarding the optimization of the second FI pre-concentration system, the effect of the particle size of the XAD resin was investigated. Obtained results show a significant increase in the efficiency of pre-concentration when the particle size diminishes.

A Box–Behnken experimental design [22] was employed for the optimization of the lanthanum concentration (A), pH (B) and loading flow rate (C). Assayed values ranged between 10 and 42 mg l^{-1} for (A), 8 and 9.4 for (B) and 1 and 5 ml min^{-1} for (C). A set of standard solutions of 1.0 $\mu\text{g l}^{-1}$ of tellurium with the different lanthanum concentrations was prepared. Buffer solutions, which were adjusted to the suitable pH by addition of 0.2 M ammonia, were added on-line.

The experimental design shows that two factors (A and B) are significant at the 95% confidence level. The model explains 96.0% of the variability. No correlation with the other variables was found.

The highest analytical signal (absorbance) was found at pH and lanthanum concentration values ranging between 8.6–8.9 and 18–32 mg l^{-1} , respectively (see Fig. 3).

Once found the optimal conditions for the flow injection systems, experiments were performed in order to evaluate the on-line coupling of both alternatives to the discrete analyzer. Whilst a successful on-line operation was obtained with the Dowex system (the complete procedure is described in Experimental section), serious problems were found for the XAD-4 system. An increase of the internal pressure during the washings of the micro-column between injections forced us to work under off-line conditions.

It is important to remark that, at the selected flow rate, the contact time sample/resin is short and the complete retention of the analyte is not possible. Consequently recoveries fall below 100% and both, standards and samples, need to be pre-concentrated and eluted under identical conditions.

The main features of both FI procedures are listed in Table 3.

3.2. Analytical performance

The figures of merit for tellurium determination *via* the two alternatives presented in this work are summarized in Table 4.

In order to test the accuracy and applicability of the proposed methodologies to the analysis of real samples, the standard reference material (SRM) 1643e from NIST (trace elements in water) was employed for the XAD system. Obtained results, as the average of four separate determinations, are shown in Table 5. As it can be seen, Te concentration is in good agreement with the certified value (95% confidence level).

In the case of the Dowex system, recovery experiments were carried out in order to investigate the goodness of the proposed methodology. Tap water samples were spiked with three different concentrations of tellurium and then analysed. Obtained results show values ranging between 95 and 101%, demonstrating the suitability of the methodology.

Additionally, the system was employed to determine total tellurium in drinking mineral waters from different geographic locations (Pampeana plain and Andes mountain chain). The concentration of tellurium was below the limit of detection.

4. Conclusions

The use of Dowex 1X8 as material filling fulfills the requirements for the on-line operation of the FI-GFAAS system. In this way, it is possible to perform the fully automatic determination of ultra-traces of tellurium in tap water. The material suffers no compaction during the pre-concentration cycles and thus, a long-term operation of the column (about 50 cycles) is assured. However, the low selectivity of the anionic exchange resin constrains its use in saline samples.

On the other hand, Amberlite XAD shows a higher level of tolerance to the presence of dissolved ions. But neither automatic operation nor long-term use of the adsorbent resin are possible due to its severe compactation during the default sequence of washing of the GF autosampler. Further work will be conducted to test a mixing of the resin with some kind of inert solid (washed silica for example) in order to diminish the internal pressure inside the micro-column.

Regarding speciation analysis, up to now, it was not possible to find a pH window for distinctive pre-concentration or for distinctive elution of tellurite and tellurate, either with Dowex 1X8 or with Amberlite XAD.

Acknowledgment

The authors thank the program of Science and Technology of Buenos Aires University (UBACyT), CONICET and INQUIMAE for financial support.

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