



Technical note

Increasing the sensitivity of electrochemical generation of volatile Te species

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ABSTRACT

Vapor generation is a very sensitive sample introduction technique for the determination of hydride forming elements by atomic spectrometry. However, the drawback of Te determination using vapor generation methods lies in the low stability of the volatilized Te species. We report a sensitive method for the determination of Te(IV) based on electrochemical vapor generation and atomic fluorescence spectrometry. Transport losses were reduced and sensitivity of the method was improved by cooling the gas-liquid separator and by using a mix of Ar and H₂ as the stripping and carrier gas. The limit of detection, repeatability and generation efficiency are 0.14 ng mL⁻¹, 2.1% and 79%, respectively.

1. Introduction

Tellurium is a non-biogenic metallic element toxic to both microorganisms and higher organisms [1]. Its ecological impact will grow, because it is widely used in rewritable CDs and DVDs and in semiconductor technology including CdTe solar panels [2,3]. In addition, experiments simulating landfill conditions showed that tellurium can be leached from solar panels deposited on landfills into the environment [4]. Thus, the risk of exposure to Te grows and methods for trace and ultratrace determination of Te in various matrices are required. Dissolved Te can be determined in samples at trace and ultratrace levels using electrochemical and spectroscopic methods. The most sensitive methods nowadays include inductively coupled plasma mass spectrometry (ICP-MS) or vapor generation coupled to atomic fluorescence spectrometry (AFS) or ICP-MS [5,6]. Vapor generation techniques based on the determination of TeH₂ or other volatile species are a logical choice because of inherent separation of the analyte from the sample matrix. [7] Recent renewed interest in Te determination using vapor generation includes electrochemical (EcVG) [8] and UV-photochemical vapor generation (UV-PVG) methods. [5,6,9,10]. EcVG has been developed to overcome the drawbacks of chemical hydride generation (CHG), namely the problems associated with the limited stability of the reducing agent, NaBH₄. Reduction of the analyte and production of H₂ in EcVG are achieved using electric current in a mineral acid medium. Fundamentals, working conditions and advantages of EcVG were summarized in two review articles. [11,12] EcVG presents a suitable compromise between CHG, which is more expensive, and UV-PVG, which is simpler, cheaper, environmentally friendly but very sensitive to the presence of acids and salts [13] present in the sample

matrix naturally or added during the sampling as preserving agent.

Te forms less stable volatile species than its lighter analogue Se, thus requiring optimization of transport conditions as well as generation conditions for successful application of vapor generation methods [8]. This paper proposes simple and sensitive determination of Te based on EcVG (generation efficiency 75%) and carefully controlled volatile species transport conditions.

2. Materials and methods

2.1. Reagents and materials

Electrolytes were prepared from H₂SO₄ and HCl (both Suprapure purity; Merck, Germany). Deionized water purified by MilliQ_{PLUS} system (Millipore, USA) was used throughout. Stock solution containing 100 mg L⁻¹ of Te(IV) was prepared from sodium tellurite (Sigma-Aldrich, USA). Catholytes and anolytes were prepared by dilution of the appropriate concentrated acids or stock solutions of salts: HCl (Fluka Analytical, Austria), H₂SO₄ (Merck, Germany), H₃PO₄ (LachNer, Czech Republic), NaCl (Suprapure Grade, Merck, Germany), Na₂SO₄ and NH₄Cl (both from LachNer, Czech Republic). Interference was evaluated using stock solutions prepared from Na₂SeO₃·5H₂O, Na₂SeO₄·10H₂O and As₂O₃ and from stock solutions (1.00 g L⁻¹) of As(III), Sb(V), Ni(II), Fe(III), Cd(II) and Pb(II) prepared either from pure metals or nitrate salts and dissolved in 0.50 M nitric acid. Stock solution of Cu(II) was prepared in 0.05 M HNO₃. Argon (99.998%) and H₂ (99.90%, both from Linde Technoplyn, Czech Republic) were used as carrier and atomization gas (AFS only).

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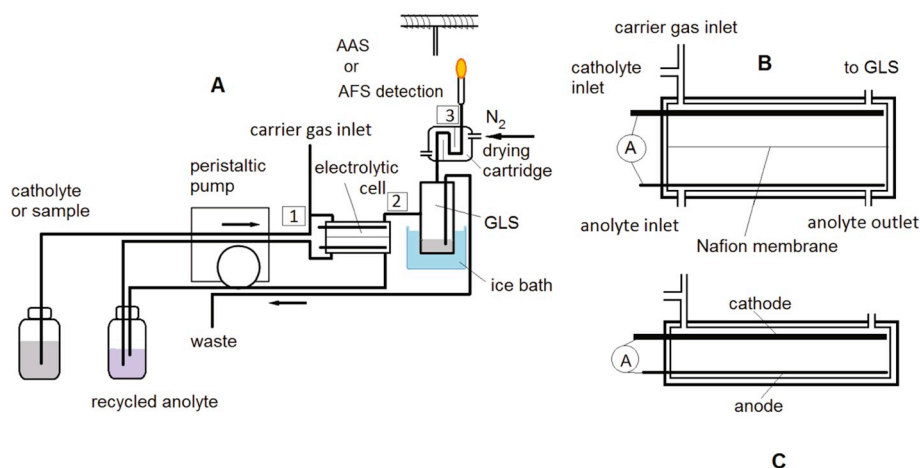


Fig. 1. Experimental set-up. Schematics show the experimental set-up (A), cell I (B) and cell II (C), AAS detection of volatile Te species in quartz furnace shown in A was used only during selection of cell type and cathode described in section 3.1 and Section S1 (Appendix), Numbers 1, 2 and 3 indicate tested hydrogen introduction points (see Section 3.4 and Section S2 (Appendix)).

2.2. Volatile species generation and detection system

The experimental set-up is shown in Fig. 1. Experiments with different electrochemical cells were carried out with AAS detection (Unicam 939, Unicam, UK) at the 214.4 nm Te line with spectral bandwidth 1.0 nm. Te hollow cathode lamp (Heraeus, Germany) was operated at 8 mA. Volatilized hydrides were atomized in quartz furnace atomizer (T-shaped, atomizer arm length 170 mm, internal diameter of the atomizer arm 5 mm, the ends of the atomizer arms are widened to 12 mm.) externally heated to 950 °C (resistance heating for quartz atomizers EHT, RMI, CR). Further method development and validation was accomplished with atomic fluorescence spectrometer Millenium Excalibur (PSA, UK) with miniature diffusion flame atomizer. The sensitivity of detection depends on the value of signal amplification represented in the PSA Millenium Excalibur by selection of GAIN. Except for Figures of Merit all measurements were carried out with GAIN 100. The quartz MDF atomizer was cylindrical, length 25 mm, i.d. = 4.5 mm, o.d. = 6.0 mm. Te superlamp was operated at 15 mA with boost current 17 mA. Liquids were pumped using a MasterFlex L/S pump (Cole Parmer, USA). Flow rates of gasses were controlled by mass flow controllers (Cole Parmer, USA). Separation of the generated volatile species from the liquid waste took place in a tubular gas liquid separator (GLS) with forced outlet and 15 mL internal volume. Partially transparent PTFE tubing was used for transport of the volatile species. The top of the miniature diffusion flame atomizer was located 2 mm below the optical path. HR-CS-AAS instrument ContraA 700 equipped with transversally heated graphite cuvette with integrated platform was used for the determination of Te remaining in the waste after generation and subsequent calculation of generation efficiency.

Two types of laboratory-made electrochemical cells were fabricated and tested. Both cells had PTFE body but cell I contained Nafion® 117 membrane dividing the cell compartments and cell II was membraneless cell. Each compartment of cell I had inner volume 0.5 mL (5 × 5 × 2 mm). The inner volume and dimensions of cell II were the same as those of the cathode compartment of cell I. Anode was always made from platinum wire (50 mm in length, 0.5 mm in diameter, purity 99.99%; Safina, Czech Republic), and cathode either from lead wire (50 mm length, 2 mm diameter, purity 99.99%; Aldrich, USA), silver wire (length 50 mm, 0.5 mm diameter, purity 99.98%; Safina, Czech Republic), or platinum wire (same as anode). Electric current was supplied by laboratory source LPS 303 (American Reliance, USA, maximum current 3.0 A and maximum voltage 30 V.) Galvanostatic set-up was used throughout.

2.3. SRM sample preparation

Sample for the validation of accuracy was prepared by evaporating

50 mL of NIST SRM 1643f (Trace Elements in Water) to near dryness and diluting it to 10 mL with deionized water to simultaneously reduce the content of HNO₃ and prepare solution with sufficient concentration to be analyzed by standard addition method. Two milliliters of the concentrated solution were transferred to 10.00 mL volumetric flasks, spiked by sodium tellurite solution and diluted by concentrated HCl and deionized water to form a series of solutions to be analyzed by the standard addition method. Solutions were measured in quadruplicates.

2.4. Analytical procedure

The measurements were carried out in a continuous mode. The catholyte and anolyte were continually pumped into the cell. Sample contained the same concentration of HCl as catholyte to maintain constant conductivity. The introduction of sample was carried out by manually switching between catholyte and sample solutions. Sample was introduced at constant flow rate until a stable steady-state signal was achieved (approximately 40 s with AAS detection and 30 s with AFS detection) followed by switching back to catholyte. New measurement was started after the baseline returned to its original value. Only one electrolyte serving as both catholyte and anolyte was used in cell II. If not stated otherwise, each sample was measured five times. The results were calculated from means of signal heights measured at steady state.

3. Results and discussion

3.1. Choosing the cell type and cathode

The first experiments were aimed at finding a suitable combination of cell type, electrolyte and cathode material and were carried out with quartz furnace AAS detection. Two types of cells were tested. Cell I was a common thin layer type [14] with cathode and anode compartments separated by a Nafion® 117 membrane (thickness 0.007 in.) preventing reaction between products of cathodic reduction and anodic oxidation. Anolyte in thin layer cell type can be recycled during the measurement to reduce the amount of produced hazardous waste. Cell II was a membraneless type having only one compartment containing both electrodes. Simplified construction is offset by the risk of decomposition of the generated hydride by oxidizing products evolved on the anode and corresponding risk of lower generation efficiency [15]. Optimization of reaction conditions is, therefore, even more crucial than with the membrane cell.

We tested three electrolytes (HCl, H₂SO₄ and H₃PO₃) and two cathode materials (Pt, Pb) with cell I and five electrolytes (NaCl, Na₂SO₄, HCl, H₂SO₄ and NH₄Cl) and three cathode materials (Pt, Ag, Pb) with cell II. The optimum combination for cell II (Pt cathode, 1.0 M

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