Technical Note

Electrochemical generation of volatile form of cadmium and its in situ trapping in a graphite furnace

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ARTICLE INFO

ABSTRACT

This publication describes the combination of flow-through electrochemical generation (EcVG) of cadmium volatile form with its in situ trapping in a graphite furnace atomizer. Three cathode materials (Pt, Pb, and Ti) and four potentially suitable electrolytes (HCl, H_2SO_4, HCOOH and NaCl) were tested. Automated sampling equipment for the graphite furnace atomizer with an untreated fused silica capillary was used for the introduction of the cadmium volatile form into the iridium-treated graphite furnace. The limit of detection (LOD) of the electrochemical Cd volatile form generation with in situ collection was 1.0 ng ml^{-1} (concentration LOD) or 1.5 ng (absolute LOD). The efficiency of the method was estimated and discussed. The effect of selected concomitant ions was evaluated and the accuracy of the proposed method was established by determination of the Cd content in the NIST SRM 1643e certified reference material.

1. Introduction

Vapor generation coupled with atomic spectroscopic methods has been a routine technique for the determination of As, Bi, Ge, Hg, Sb, Se, Sn, Te, and Pb for several decades [1]. Furthermore, in recent years, the scope of volatile compounds generation has been expanded to include the determination of transient metals [2].

The principal advantages of gas phase sample introduction lie, firstly, in the separation of the analyte from the sample matrix and, secondly, in higher introduction efficiency compared to liquid nebulization [3]. A conventional and widely applied approach to the generation of volatile compounds is chemical reduction using NaBH$_4$ [4]. However, there also exists a simpler alternative approach utilizing electrochemical reduction to avoid the use of a chemical reductant [5]. The most significant advantage of the electrochemical generation of volatile compounds (EcVG) is the elimination of the use of sodium tetrahydroborate reagent, which is expensive, unstable and represents a potential source of contamination [6,7]. Other advantages of electrochemical generation compared to chemical generation include a reduction in interferences from concurrent transition metals and decreased influence of the oxidation state of the analyte on the volatile form yield [8].

Cadmium is a heavy metal, toxic principally to the kidneys and liver and with accumulative properties in living organisms. It is commonly used in manufacturing of zinc-cadmium batteries and in metallurgy for anti-corrosion surface treatments [9,10]. Cadmium levels in the environment are gradually increasing and therefore sensitive and selective methods for its determination are desirable.

Various approaches to the generation of volatile compounds (mostly chemical, electrochemical and, recently, also photochemical generation of the volatile form) have been applied to the determination of cadmium coupled with various element-specific detectors. These included quartz furnace atomic absorption spectrometry (QFAAS) [11–14], trapping on quartz and subsequent revolatilization and atomization in QFAAS [15], in situ trapping flame AAS [9], electrothermal atomic absorption spectrometry (ETAAS) [16–22] and atomic fluorescence spectrometry (AFS) [23,24]. However, the number of publications dealing with electrochemical generation of the cadmium volatile form is still limited. The first paper published on this subject was by Arbab-Zavar [12] and it proposed the electrochemical generation of the cadmium volatile form in a batch generator. The authors continued to study this subject in a mechanistic study [25]. Two recent publications from the same research group describe electrochemical generation of the cadmium volatile form in a flow injection arrangement for the determination of the cadmium content in water samples [11,13]. Zhang et al. coupled electrochemical generation of the cadmium volatile form in a continuous flow arrangement with AFS detection for the determination of cadmium content in rice [24]. In 2011, Masrournia described coupling of batch electrochemical generation of the cadmium volatile form with its in situ collection and ETAAS determination [19].

In situ collection of volatile compounds in a graphite furnace introduces the possibility of further decreasing the limits of detection. A graphite furnace is used to decompose the volatile compound and trap the analyte species on the tube surface, thereby effecting rapid separation of the analyte from the remaining sample matrix as well as its collection [4]. Several materials have been successfully employed for trapping and the subsequent release and determination of cadmium, e.g. Pd [20], Ir [21], Ir + Rh [26,27], W [21] and W + Rh [28] coated

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graphite tubes as well as uncoated graphite tubes [22] have been used. This paper is focused on the development of a combined flow-through EcVG-in situ trapping ETAAS method for the determination of cadmium in water samples, which (as far as we could determine) has not yet been published.

2. Experimental

2.1. Standards and reagents

Deionized water prepared by the Milli-Q Plus system (Millipore, USA) was used throughout the measurements. Hydrochloric acid (suprapure grade, Merck, Germany) diluted to 0.5 mol dm^{-3} served as the catholyte solution and 2.0 mol dm^{-3} sulphuric acid (research grade, Merck, Germany) as the anolyte solution. Argon of 99.998% purity (Linde, Czech Republic) was used as the carrier gas. A standard solution of Cd(II) (1.000 ± 0.002 g l^{-1}, Merck, Germany) was used for preparation of the Cd(II) solutions by dilution with an appropriate amount of the catholyte solution. Ammonium hexachloroiridate(III) monohydrate (Sigma-Aldrich, USA) was used to prepare the 1.0 g l^{-1} Ir(III) solution, which was used for permanent modification of the graphite tube inner wall (see Appendix A, Section S3).

Surfactants were used to increase the efficiency of the Cd determination: sodium dodecyl sulfate (SDS; Serva, France; Mr = 288.37), N-(α-carbethoxypentadecyl)trimethyl ammonium bromide (Septonex; Spofa, Czech Republic; Mr = 422.48) and p-octyl(phenyl)polyoxyethylene (Triton X-100, Merck, Germany; Mr = 646.86), as well as Co(II) (Merck, Germany) and thiourea (Sigma-Aldrich, USA). The addition of Antifoam B Emulsion (Sigma-Aldrich, USA) was used to suppress foaming for surfactant concentration exceeding its critical micellar concentration. A solution of NaBH$_4$ 0.5% (m/v) (Merck, Germany) in 0.4% KOH (Lachema, Czech Republic) was used as the reducing agent for the chemical generation of the cadmium volatile form.

The effect of concomitant ions on the determination of Cd was evaluated using solutions of As (III), Se (IV), Pb (II), Hg (II), Ni (II), Fe (III), Cu (II) (all prepared from stock solutions in 0.5 mol dm^{-3} HNO$_3$, Analytika, Czech Republic), HNO$_3$ (Merck, Germany) and nitrate solution prepared from solid KNO$_3$ (Lachner, Czech Republic).

2.2. Instrumentation

A Solaar 939 atomic absorption spectrometer (Unicam, UK) equipped either with a GF 90 graphite furnace atomizer or an externally resistance-heated (EHT, RMI, Czech Republic) quartz furnace atomizer (T-shaped, optical axis arm length 120 mm and internal diameter 8 mm, inlet arm length 100 mm and internal diameter 5 mm) was used in this work. Total pyrolytic graphite tubes with extended lifetime (Unicam, UK) were employed as atomizers in the ETAAS. The inner surface of the graphite furnace was modified with a permanent Ir modifier. Either a cadmium hollow cathode lamp (Cathodeon, UK) run at 6 mA or a Photron Superlamp (Photron, Australia) run at 6 mA (boost current 4 mA) was used as the radiation source. Measurements were carried out at the 228.8 nm resonance line (0.5 nm bandwidth). Deuterium background correction was employed throughout. A laboratory source LPS 303 (I_{max} = 3 A, U_{max} = 30 V) (Taipei Hsien, Taiwan) provided constant current for the electrochemical generation cell. A computer-controlled MasterFlex L/S peristaltic pump (Cole-Parmer, USA) equipped with an eight-channel/eight-roller Ismatec head was used for pumping and withdrawing all the solutions. The electrochemical generator was a laboratory-made thin-layer flow-through cell described in detail in [29] as cell I and also in Section S1 of the supplementary material (Appendix A). Chemical vapor generation was carried out by replacing the electrochemical cell by a reaction coil made from PTFE capillary (i.d. 0.8 mm, 1000 mm length). Instead of the catholyte, either acidic blank solution or acidified sample solution was pumped into the reactor and the NaBH$_4$ solution was pumped through the anolyte branch. Both channels were connected directly before the reaction coil and prior to the introduction of the carrier gas. The laboratory-made quartz sampling equipment for ETAAS used in this project was already described in detail in the previous publication [29] and details are also included in the supplementary material (Appendix A, Section S2).

2.3. Instrumental setup

The instrumental setup is shown in Fig. 1. Tygon tubing (Cole-Parmer, USA) with 1.02 mm and 0.57 mm internal diameters was used for pumping all the solutions. A gas–liquid separator with forced outlet (cylindrical shape, top inlet, height 60 mm and diameter 21 mm) was employed for separation of the cadmium volatile form from the liquid waste. Teflon tubing with an internal diameter of 0.8 mm was used for the connection between the outlet of the electrochemical cell and inlet of the gas–liquid separator (length 30 mm) as well as between the outlet of the gas–liquid separator and the externally heated quartz furnace atomizer (total length 100 mm) or ETAAS sampling device (total length 150 mm). The quartz furnace atomizer was operated in continuous flow mode with direct detection (via AB in Fig. 1). Some modifications of the basic instrumental setup with direct detection were made to study the influence of various additives on the sensitivity of the cadmium determination. Solutions of surfactant/antifoam/reagents were introduced in three parts of the instrumental setup (denoted in Fig. 1 and described in detail in Section 3.3). To test the influence of increased temperature on the Cd determination, the setup for the on-line atomization in the quartz furnace was modified by connecting the outlet from the gas–liquid separator directly to the atomizer inlet arm by a quartz capillary (50 mm, no solenoid valve). The upper part of the gas–liquid separator, the capillary and the atomizer inlet arm were heated by a resistance wire (Kanthal, R = 4.2 Ω/m, o.d. = 0.65 mm, ELCHEMCo, Czech Republic) coiled around the capillary and the atomizer inlet arm. The temperature (varied in the range 50 °C–250 °C) was measured on the capillary by an infrared thermometer Voltcraft IR-1200 (Voltcraft, Germany).

2.4. Procedure and temperature program

The catholyte solution (0.5 mol dm^{-3} HCl) was continuously pumped through the cathode chamber of the electrochemical cell at a flow rate of 3.0 ml min^{-1}. The Ar carrier gas (23 ml min^{-1}—in situ trapping ETAAS mode; 25 ml min^{-1}—QFAAS direct detection mode) was introduced into the catholyte stream before entering the inlet port of the electrochemical generator. The anolyte solution (2.0 mol dm^{-3} H$_2$SO$_4$) was continuously pumped at a flow rate of 1.0 ml min^{-1}. The cadmium volatile form with excess hydrogen, the carrier gas and liquid waste were subsequently transported to the gas–liquid separator. The separated gases were directed from the gas–liquid separator to the externally heated quartz furnace atomizer (direct detection mode, via AB in Fig. 1) or to the graphite furnace (trapping mode, via AC in Fig. 1). A very similar procedure was employed for the chemical generation of the cadmium volatile form (with only direct detection in QFAAS). The acidified blank (HCl, 0.001 mol dm^{-3}) or sample was pumped at a flow rate of 3.0 ml min^{-1} and the reducing agent (NaBH$_4$, 0.5 mol dm^{-3}) was merged with it at a flow rate 1.0 ml min^{-1}. Ar was introduced immediately after this merging. The optimum generation and determination conditions are summarized in Table 1.

The graphite furnace temperature program used for the collection/atomization of the cadmium volatile form is described in Table 2. The peak absorbance (peak height) was used to evaluate the influence of the experimental parameters and later for evaluation of the influence of the concomitants on the determination of Cd. The integrated absorbance (peak area) and the peak absorbance data were used to