



Flow injection electrochemical hydride generation atomic absorption spectrometry for the determination of cadmium in water samples

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ABSTRACT

A new flow injection method coupled to an electrochemical hydride generator with atomic absorption spectrometry was proposed for determination of cadmium. The influence of the experimental parameters such as cathode material, catholyte type, sample volume, catholyte flow rate, temperature of the atomizer, catholyte concentration, carrier gas flow rate, electrolytic current and cathode surface area on the analytical response was studied. Under the optimized conditions, the calibration curve was linear in the range of 2–50 ng mL⁻¹ of Cd. A concentration detection limit ($3\sigma_b$, $n=9$) of 0.61 ng mL⁻¹ Cd and a relative standard deviation of 5.1% (RSD, $n=9$) for 20 ng mL⁻¹ Cd were obtained. The potential interferences from various ions were also evaluated. The accuracy of the method was verified by the determination of cadmium in a certified reference material. The calculated concentration of Cd in CRM was found to be in good agreement with the certified value.

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1. Introduction

Chemical hydride generation (CHG) as sample introduction technique has been coupled with different atomic spectrometric detections for determination of trace concentrations of hydride forming elements (HFEs) i.e., As, Bi, Ge, Sb, Se, Sn, Te and Tl, performed by reaction of acidified sample with sodium or potassium tetrahydroborate (III) [1–3]. More recently, similar to the well-known CHG technique and cold vapor generation method for Hg [2] and Cd [4], chemical vapor generation (CVG) has also been successfully employed in atomic spectrometry for the formation and detection of unknown gaseous species, probably as volatile hydrides, free atoms or nanoparticles of some transition and noble metals [5–7]. However, the precise identification of these species has not yet been established except for Hg and Cd which are elemental [2,5,7].

In the specific case of cadmium, several systems have been developed for generation of volatile Cd species as a cold vapor, individually [8–13] or simultaneously with other metals [14–18] and have been effectively coupled with quartz tube atomizer (QTA) [8,14] or in-situ trapping (ET) [12,16] atomic absorption spectrometry (AAS), in-situ trapping flame AAS [18], inductively coupled plasma (ICP) atomic emission spectrometry (AES) [10,15] or mass spectrometry (MS) [13,17] and atomic fluorescence spectrometry (AFS) methods [9,11].

As a suitable alternative approach to CHG techniques, electrochemical hydride generation (ECHG) has been widely used as a sample introduction method for spectrometric determination of Hg [19–22] and hydride forming elements, such as, As [19,23–26], Bi [19], Cd [27–30], Ge [19,26], Pb [31], Sb [19,23,25,26], Se [19,23–26], Sn [25,26,32], Te [33], Tl [34] and Zn [35] because of its advantages. The ECHG technique requires only acids that can be obtained in high purity and eliminates the use of sodium (or potassium) tetrahydroborate reagent which is expensive, unstable and susceptible to contamination. The method is based on the reaction between electrochemically generated hydrogen atoms on the cathode surface of electrolytic cell and HFEs [36,37]. ECHG procedures have been performed in batch (B) [27,31,32,34,35], continuous-flow (CF) [21,22,26,33] and flow-injection (FI) [19,23–25] systems. Using FI methods, high sample throughput, improved precision, low sample and reagent consumption, low operation cost, easy automation and reduced potential contamination as well as decreased interferences could be achieved.

In our earlier work, an ECHG system using semi-batch technique (B-ECHG), the cadmium hydride was generated and determined by AAS. It was found that the system produced sensitive and reproducible signals for trace amounts of cadmium. However, the batch method had a number of disadvantages. Its throughput was restricted by the time needed for the replacement of the cathode and sample after each measurement cycle and reduced to 10 h⁻¹. The B-ECHG technique was time-consuming and more prone to interferences [27]. Recently, Zhang et al. reported a continuous-flow ECHG method for the determination of cadmium with AFS [30].

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The aim of this work is to study the influence of relevant experimental parameters on Cd determination performed by a flow injection electrochemical hydride generation atomic absorption spectrometry (FI-ECHG-AAS) which coupled a laboratory-made electrolytic cell as a generator to an electrically-heated quartz tube AAS. In addition, the susceptibility of interference from various ions was evaluated.

2. Experimental

2.1. Instrumentation

A Shimadzu 680 atomic absorption spectrometer (Shimadzu, Japan) equipped with an electrically-heated quartz tube atomizer (QTA, 150 mm length, 4.2 mm i.d.) was used for atomic absorption measurements. Cadmium hollow cathode lamp (Hamamatsu Photonics, Japan) operated at 4 mA was used as radiation source at a wavelength of 228.8 nm with 0.3 nm bandpass. In-house software permitted the virtualization and evaluation of transient signals. The pH measurements were made using a Crison pH meter (Crison Instruments, Spain).

2.2. Electrochemical hydride generation system

The home-made electrolytic flow-through cell similar to that described in our previous work [29] was used to evaluate the electrochemical hydride generation (ECHG) of Cd. Fig. 1 shows the expanded design of the electrolytic hydride generator. The cell consists of cathodic and anodic compartments (both $40 \times 6 \times 4$ mm³, inner volumes of 1.0 mL) separated by a Nafion cation ion-exchange membrane (DuPont Co., USA). A Pb–Sn wire (Pb:Sn 37:63, diameter of 0.80 mm, Asahi, Singapore) and a coil of platinum (0.25 mm diameter, Merck, Germany) were used as the cathode and anode, respectively. An injection valve (PIV1, Sabz Zist Kimiya Co., Iran) was used to inject standards and samples. A Minipuls-3 peristaltic pump (Gilson, France) and a four-channel head were employed to transport the electrolytes and samples and withdraw the effluent. A programmable DC power source (Promax, FA-851, Promax Electronica S.A., Spain) was used as a constant current supply for the electrolytic cell. The carrier solution and the gaseous products from the cathode as well as the argon carrier gas stream controlled by a flow meter (Emerson Electronic co., USA) were transported into a laboratory-made gas–liquid separator (GLS, 10 mm

i.d., 38 mm length). Consequently the generated volatile compounds were transferred through a 20-cm-long PVC tube (3.1 mm i.d.) to the atomizer, placed directly in the optical path of the atomic absorption spectrometer. The connections were made by PVC tubing (2.05 mm i.d.).

2.3. Reagents and materials

All reagents used in this work were of analytical grade (Merck, Germany). A standard stock solution of 1000 mg L^{-1} Cd was prepared by dissolving appropriate amounts of CdCl_2 in ultrapure water. Working solutions were prepared by dilution of stock standards with dilute NaCl solution. Doubly-distilled water was used throughout. All solutions containing the potential interfering ions studied were prepared by adding appropriate amounts of stock solutions made from their corresponding salts in dilute NaCl (0.020 mol L^{-1}). Argon with 99.999% purity was used as the carrier gas.

2.4. Operating procedures

Electrochemical hydride generation was performed in flow injection mode operated as follows: The blank carrier catholyte and anolyte solutions were continuously pumped into the cathode and anode chambers of the cell, respectively, at a flow rate of 6.0 mL min^{-1} by a peristaltic pump. The anolyte ($0.50 \text{ mol L}^{-1} \text{ Na}_2\text{CO}_3$) was circulated and could be used for several days. At the same time, the cadmium sample was injected into the sampling loop of the injection valve at the same flow rate. If not stated otherwise, the standard sample was a solution of 50 ng mL^{-1} Cd in 0.010 mol L^{-1} NaCl and the carrier was pure 0.010 mol L^{-1} NaCl (blank catholyte). The effluent was discharged from the GLS at a flow rate of 8 mL min^{-1} . After about 3–4 min electrolysis time, injection of 1.0 mL sample into the catholyte carrier stream was performed manually via an injection valve and the sample was propelled to the cell. The sampling valve can be switched between the injection and loading positions every 30 s. The carrier gas at a flow of 100 mL min^{-1} was introduced into the carrier stream before entering the input port of the electrochemical generator and has led the electrochemically generated products (Cd vapor and hydrogen) into the gas–liquid separator where the hydrides and the liquid were separated. The generated volatile species with excess hydrogen were directed by the argon carrier gas to the electrically-heated quartz tube atomizer adjusted at 860 ± 10 °C for the atomic absorption detection. The transient peak-shaped absorbance signals were recorded and the peak heights were used as the analytical responses. Error bars shown in all figures represent the standard deviation of three replicate determinations. A complete cycle of the procedure lasted approximately 60 s. The analytical throughput was about 45 h^{-1} .

3. Results and discussion

3.1. Optimization of the experimental parameters

3.1.1. Cathode material

It is generally believed that the ECHG technique is carried out by the reaction of the electrochemically-generated hydrogen atoms and the reduced analyte on the cathode surface [36,37]. The electrolytic formation of cadmium hydride needs a high negative redox potential [38], so it is necessary to use cathode materials with high hydrogen overvoltage.

Some materials such as Pt wire, graphite rod, Pb and Sn bars and Pb–Sn wire were examined as cathode at a surface area of about 1 cm^2 for each electrode. The experiments indicated that it was not possible to obtain any detectable cadmium absorbance signal using Pt cathode. The signals generated using other cathode materials were negligible except that for Pb–Sn alloy. This may be related to its unstable surface under the applied electrolytic conditions. The simultaneous production of lead and tin hydrides and the hydrogen contributed to

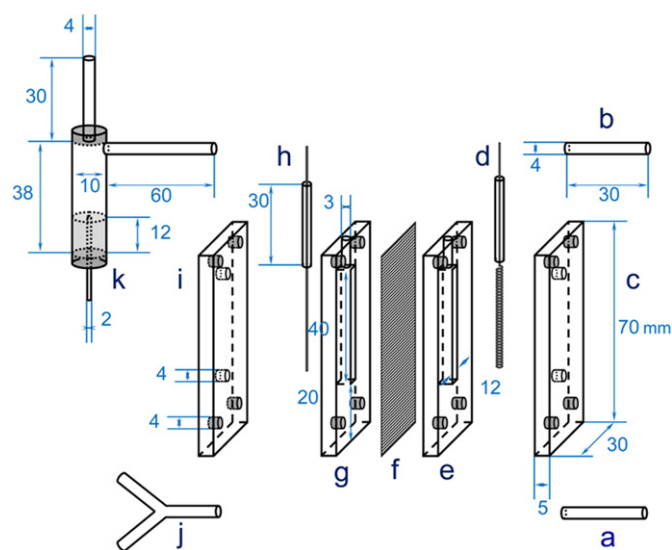


Fig. 1. Expanded view of the flow through cell and the design of the gas liquid separator (GLS); a and b, connectors of the anolyte flow; c, e, g and i, cell bodies; d, anode; h, cathode; f, Nafion membrane; j, Y-shaped connector for the catholyte and Ar flow in; k, GLS.

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