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Determination of antimony by using a quartz atom trap and electrochemical hydride generation atomic absorption spectrometry

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Abstract

The analytical performance of a miniature quartz trap coupled with electrochemical hydride generator for antimony determination is described. A portion of the inlet arm of the conventional quartz tube atomizer was used as an integrated trap medium for on-line preconcentration of electrochemically generated hydrides. This configuration minimizes transfer lines and connections. A thin-layer of electrochemical flow through cell was constructed. Lead and platinum foils were employed as cathode and anode materials, respectively. Experimental operation conditions for hydride generation as well as the collection and revolatilization conditions for the generated hydrides in the inlet arm of the quartz tube atomizer were optimized. Interferences of copper, nickel, iron, cobalt, arsenic, selenium, lead and tin were examined both with and without the trap. 3σ limit of detection was estimated as 0.053 μg l^{-1} for a sample size of 6.0 ml collected in 120 s. The trap has provided 18 fold sensitivity improvement as compared to electrochemical hydride generation alone. The accuracy of the proposed technique was evaluated with two standard reference materials; Trace Metals in Drinking Water, Cat # CRM-TMDW and Metals on Soil/Sediment #4, IRM-008.

Keywords: Electrochemical hydride generation; Antimony; Preconcentration; Quartz trap; Atomic absorption spectrometry

1. Introduction

Hydride generation (HG) is a gas phase sample introduction technique for atomic spectrometry and finds widespread application for determination of elements like As, Sb, Se, Sn, Te, Bi, Ge and Pb at trace levels in many sample types. Chemical HG involves the conversion of analyte in an acidified solution, to its gaseous hydride by a reducing agent, mostly sodium tetrahydroborate, under ambient conditions. The popularity of HG is due to the advantages it offers; the most significant of which are increased transport efficiency and separation of analyte from the matrix which enables preconcentration as well as suppression of the interferences [1].

Electrochemical HG has been proposed as alternative to chemical HG [2–4]. In electrochemical HG, the hydride is formed in the cathode compartment of an electrochemical cell. The generation process is considered to take place in sequential steps: deposition of the analyte on the surface of the cathode, reduction of the analyte and formation of hydrides followed by their desorption. The most significant advantage of electrochemical HG systems is the elimination of the use of sodium tetrahydroborate reagent which is expensive and a potential source of contamination. In addition, solutions of this reagent slowly decompose producing hydrogen. Other advantages of electrochemical HG include reduction of interferences from transition metals as compared to chemical HG and the reduced influence of the oxidation state of the analyte on the hydride yield, depending on the type of cathode material used [5].

In recent years, quartz surface has been used as a preconcentration medium for hydrides generated in flow systems. A feasible collection and revolatilization method was first reported for Pb [6] followed by Sb [7,8] and Cd [9]. The trapping medium was formed by external heating of either the inlet arm of the quartz tube atomizer or a separate cylindrical quartz tube. Generated analyte species were trapped on quartz surface heated to the collection temperature and the collected species were revolatilized when the trap was heated further to releasing temperature and hydrogen gas was introduced in the trapping medium. Either the conventional quartz T-tube [6,9] or

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multiple microflame quartz tube [7,8] were employed as atomizers. With the suggested technique, it is possible to analyze samples without time-consuming and potentially contaminating preconcentration procedures. These works proposed simple and inexpensive devices with comparable detection limits to those obtained with *in-situ* trapping of hydrides in graphite furnace.

In our earlier work, a preliminary evaluation on preconcentration of stibine on quartz surface was presented [7]. In the present work, we further investigated the analytical performance of the trap, in particular regarding the interferences. In addition, SbH_3 was generated using electrochemical HG technique. A thin-layer electrochemical flow through cell was constructed with a lead cathode. Interferences of selected transition metals and other hydride forming elements were examined with and without trapping. Finally, in order to check the accuracy of the proposed system, analysis of standard reference materials were performed.

2. Experimental

2.1. Reagents

All reagents used were of analytical grade. Standard solutions, used as the catholyte, were prepared by appropriate dilution of the 1000 mg l^{-1} Sb(III) stock solution (Ultra Scientific) with 1.0 mol l^{-1} HCl (Merck). 100 ml of 500 mg l^{-1} Sb (V) stock solution was prepared by dissolving 0.116 g of potassium antimonite, $KSb(OH)_6$.1/2 H_2O, (Aldrich) in deionized water and Sb(V) standard solutions were prepared from this stock solution. The anolyte solution was 2.0 mol l^{-1} H_2SO_4 (Carlo Erba). 0.5% (m/v) $NaBH_4$ (Merck) in 0.4% (m/v) NaOH (Carlo Erba) was used for chemical hydride generation. For the interference studies, standard solutions of Ni(II), Co(II), Cu(II), Fe(III), As(III), Se(IV), Sn(II) and Pb(II) were prepared from the 1000 mg l^{-1} stock solutions (Aldrich) of the corresponding element in 1 mol l^{-1} HCl. Deionized water from Milli-Q Water Purification System was used throughout the experiments.

2.2. Instrumentation

A Pye Unicam PU 9200 atomic absorption spectrometer equipped with a 50 mm air acetylene burner head was used throughout the study. Photron Sb hollow cathode lamp with an operating current of 9 mA was used as the radiation source. The analyses were done at a wavelength of 217.6 nm and 0.2 nm spectral bandwidth, employing deuterium lamp background correction.

2.3. Electrochemical cell and hydride generation system

The thin layer flow through electrochemical cell was modified from a previously reported design [10]. The cell had a Plexiglas body. It was made up of two blocks which have cathode and anode chambers embedded in them. Both of the chambers had dimensions of 100 mm × 3 mm × 3 mm and inner volume of 900 μL when the electrodes were not in place. Nafion 117 (Aldrich) was placed between the two blocks as the ion exchange membrane. The electrodes used were lead (99.9995%, Aldrich) and platinum (99.9995%, Altın Yıldız İthalat–İmalat, İstanbul) as cathode and anode, respectively. Eight screws were used to hold the two blocks tightly in order to prevent leakage. 4 holes were drilled to the sides of the plexiglass blocks at an angle of 45° as solution inlets and outlets (Fig. 1). Polytetrafluoroethylene capillary tubings (Cole Parmer) with 0.8 mm inner diameter were connected to the inlets and outlets of cathode and anode chambers with 1/16 inch tubing fittings (Cole Parmer). The same kinds of capillary tubings and fittings

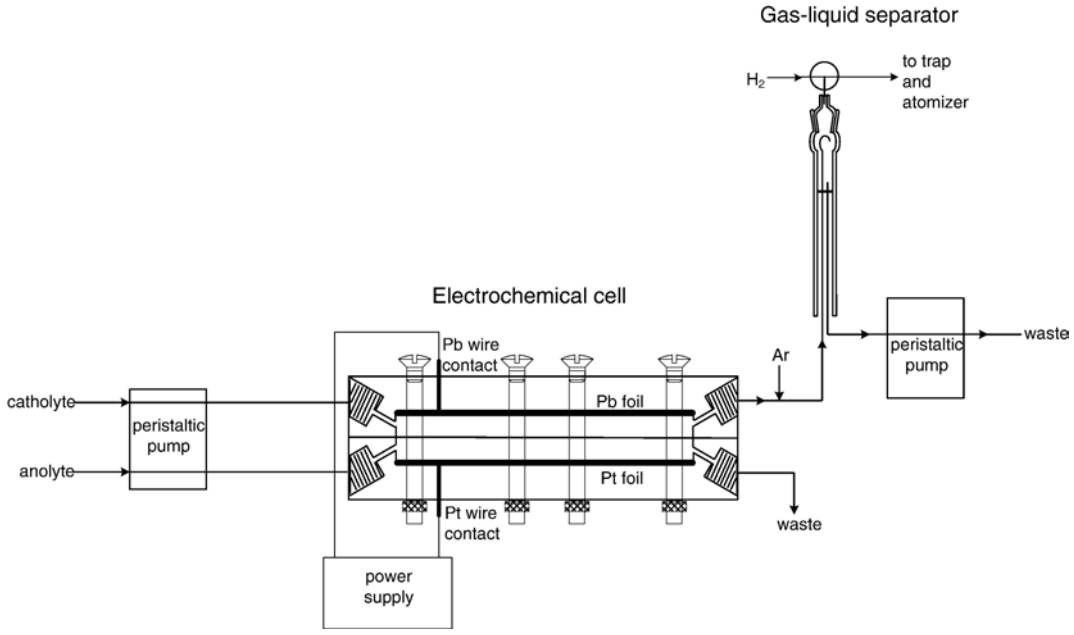

Fig. 1. Hydride generation set-up with side view of electrochemical cell.