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On-line lab-in-syringe cloud point extraction for the spectrophotometric determination of antimony ☆

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ABSTRACT

Most of the procedures for antimony determination require time-consuming sample preparation (*e.g.* liquid–liquid extraction with organic solvents), which are harmful to the environment. Because of the high antimony toxicity, a rapid, sensitive and greener procedure for its determination becomes necessary. The goal of this work was to develop an analytical procedure exploiting for the first time the cloud point extraction on a lab-in-syringe flow system aiming at the spectrophotometric determination of antimony. The procedure was based on formation of an ion-pair between the antimony–iodide complex and H^+ followed by extraction with Triton X-114. The factorial design showed that the concentrations of ascorbic acid, H_2SO_4 and Triton X-114, as well as second and third order interactions were significant at the 95% confidence level. A Box–Behnken design was applied to obtain the response surfaces and to identify the critical values. System is robust at the 95% confidence level. A linear response was observed from 5 to 50 $\mu g\ L^{-1}$, described by the equation $A=0.137+0.050C_{Sb}$ ($r=0.998$). The detection limit (99.7% confidence level), the coefficient of variation ($n=5$; 15 $\mu g\ L^{-1}$) and the sampling rate was estimated at 1.8 $\mu g\ L^{-1}$, 1.6% and 16 h^{-1}, respectively. The procedure allows quantification of antimony in the concentrations established by environmental legislation (6 $\mu g\ L^{-1}$) and it was successfully applied to the determination of antimony in freshwater samples and antileishmanial drugs, yielding results in agreement with those obtained by HGFAAS at the 95% confidence level.

1. Introduction

Antimony is found in soil, water, and air due to anthropogenic activities. Environmental legislation establishes the maximum concentration of this species in drinking water as 6 $\mu g\ L^{-1}$ [1]. On the other hand, a drug for treatment of the tropical disease leishmaniasis is formulated with antimony(V) compounds [2]. The presence of large quantities of antimony in the body causes nausea, muscle aches, vomiting, headaches, and lethargy [3]. The most-common techniques for antimony determination are voltammetry [4], potentiometry [5], hydride-generation atomic-fluorescence spectrometry [6], absorption spectrometry [7], inductively coupled plasma-mass spectrometry [8], neutron activation analysis [9], as well as hyphenated techniques such as atomic fluorescence spectrometry coupled with chromatography [10]. However, these procedures are usually time consuming, employ expensive equipment, involve toxic reagents [8–11], and often require analyte preconcentration. Thus, the development of a rapid, simple, and low-cost procedure for antimony determination is necessary.

Flow-based systems offer numerous possibilities for chemical derivatization, sample treatment, and analyte concentration, without the need to achieve chemical equilibrium. Improved precision and sample throughput, lower risks of sample contamination, as well as the potential to develop greener analytical procedures, are other advantages. In this sense, lab-in-syringe systems [12] are attractive for on-line sample preparation due to the highly reproducible sample-processing conditions, even with microvolumes of sample and reagents. These systems combine the versatility of sequential injection analysis (SIA) for solution handling and the efficient mixing inherent to the flow-batch approach [13]; therefore, they have been successfully exploited for magnetic-stirring-assisted liquid–liquid microextraction [14,15], dispersive liquid–liquid microextraction [16], and gas–liquid separation [17].

Separation and preconcentration are often required for trace analysis. Liquid–liquid extraction is one of the most widely used approaches, but it usually generates large waste volumes, is laborious

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and time consuming [18], and is susceptible to experimental errors. Cloud-point extraction (CPE) is an alternative approach that avoids the use of toxic solvents, by exploiting a non-ionic surfactant to extract the hydrophobic species incorporated in the micelle aggregates formed when the surfactant is at an appropriate concentration and temperature [3,19–24]. To avoid tedious and time-consuming manual extraction, CPE has been coupled with flow analysis, which improves precision and sample throughput, and minimizes waste generation [20,25]. Cloud point can be induced by the salting-out effect [26] or heating [27], but retention of the surfactant-rich phase (SRP) and the inherent dilution in the elution to the detection system [20,26] are critical steps. Therefore, some approaches to direct detection in the SPR have been proposed [25,28].

The goal of this work was to develop a simple, fast, sensitive, and environmental friendly procedure for antimony determination by the pioneering exploitation of CPE in a lab-in-syringe system. Multivariate optimization (factorial and Box–Behnken designs) were exploited to identify interactions between the variables, the critical experimental parameters, and for robustness evaluation. The procedure was based on the formation of an ion-pair between $[SbI_4]^-$ complex and H^+, which is extracted by Triton X-114 and measured in the SRP. The procedure was applied to determine the total antimony content in freshwater samples and antileishmanial drugs.

2. Experimental

2.1. Apparatus

The flow system comprised an automatic buret with a 5 mL glass syringe (Sciware BU 16A, Crison) and a three-way solenoid valve coupled in the head section. An eight-way selection valve (Multiburet 4S, Crison) was coupled to the solenoid valve (Fig. 1). PTFE tubes (0.8 mm internal diameter) were used as transmission lines.

A microcomputer equipped with AutoAnalysis 5.0 software (Sciware Systems, S.L., Palma de Mallorca, Spain) was employed for controlling the active devices, as well for data acquisition and processing. A charge-coupled device multichannel spectrophotometer (Ocean Optics, Dunedin, FL, USA; model USB2000) was directly coupled to a 5 cm optical-path flow cell. Radiation from a D_2 source (Ocean Optics; model DH-2000-BAL) was conducted to the flow cell by an optical fiber. STATISTICA 8.0 software was used for treatment of the multivariate data.

A Perkin-Elmer 900Z atomic-absorption spectrometer equipped with an AS-90 autosampler and WinLab32 software (Shelton, CT, USA) was used for antimony determination per the reference procedure.

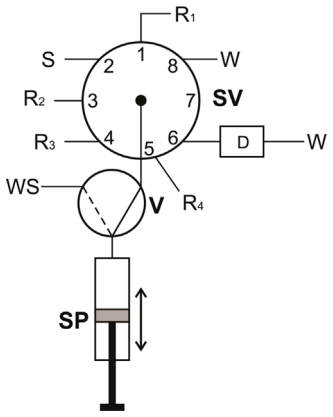

Fig. 1. Lab-in-syringe system for on-line CPE of antimony. SP: syringe pump; SV: selection valve; V: three-way solenoid valve; *D*: 5 cm optical path flow-cell coupled to the spectrophotometric detector; S: sample; R_1: 1.0 mol L^{-1} ascorbic acid; R_2: 2.0% (m/v) Triton X-114; R_3: 5.0 mol L^{-1} KI; R_4: 2.9 mol L^{-1} H_2SO_4; WS: washing stream; W: waste.

2.2. Reagents and solutions

All solutions were prepared with analytical-grade chemicals and deionized water (18 MΩ cm). Solutions 1.0 mol L^{-1} ascorbic acid (AA) and 5.0 mol L^{-1} potassium iodide were daily prepared. A 2.9 mol L^{-1} sulfuric acid solution was prepared by diluting the concentrated acid. Triton X-114 (2.0% m/v) was prepared by dilution in water. Reference solutions were prepared by dilution of antimony stock solutions (1000 mg L^{-1}) prepared from $KOOC(CHOH)_2COOSbO \cdot (1/2)H_2O$ in 0.1 mol L^{-1} H_2SO_4 or $KSb(OH)_6$ in 5.0 mol L^{-1} H_2SO_4. Water was used as the washing stream.

Freshwater samples were collected in the region of the Balearic Islands and kept refrigerated at 4 °C, after the addition of ethylenediaminetetraacetic acid (EDTA; 0.1% (m/v) to stabilize the analyte. Samples of commercially available meglumine antimoniate (labeled value: 300 mg mL^{-1}) were obtained from the local market as veterinary antileishmanial drugs. For sample preparation, the drug (17 μL) was dissolved in water (50 mL) by sonication for 10 min [29]. Then, appropriate volumes of this solution were diluted to 50 mL with water prior introduction into the flow-based system.

2.3. Flow procedure

The lab-in-syringe system employed for CPE of antimony (Fig. 1) was operated according to the routine shown in Table 1. In steps 1–4, the eight-way selection valve moved sequentially from positions 1 to 4 with simultaneous operation of the syringe pump to inject AA (500 μL), sample (2000 μL), Triton X-114 (100 μL), and KI (300 μL). Solutions were mixed inside the syringe, and a delay of 20 s was implemented for reaction development (step 5). The H_2SO_4 solution (1000 μL) was then aspirated (step 6), and the syringe was maintained in the off position for phase separation (step 7). The sample zone was then carried toward the flow cell (step 8) for the spectrophotometric measurements at 345 nm. The syringe and flow cell were then washed with water three times (step 9). Measurements were based on the peak height and carried out in triplicate. The analytical signal was based on the difference between the absorbance values measured with the reference solution (or sample) and the blank. The sample and reagent volumes indicated in Table 1 were maintained in all experiments.

2.4. Reference procedure

For accuracy assessment, the antimony content of the samples was determined by hydride-generation atomic-absorption spectrometry with on-line generation of the volatile species in a flow-based system [30], by using an aqueous solution of $NaBH_4$ (0.2% m/v) and NaOH (0.05% m/v) with HCl (10% v/v) as carrier and a 500 μL sample aliquot. An argon flow was used to carry the vapors from a gas–liquid separator to the quartz cell of the atomic-absorption spectrometer (heated by the Joule effect at 900 °C). Measurements were carried out at 217.6 nm.

Antimony (V) was previously reduced to Sb(III) by using concentrated hydrochloric acid (1 mL) and 1 mL of a 5% (m/v) KI plus 5% (m/v) AA solution to 10 mL of sample.