



Speciation of very low amounts of arsenic and antimony in waters using dispersive liquid–liquid microextraction and electrothermal atomic absorption spectrometry

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ABSTRACT

A new procedure for the determination of inorganic arsenic (III,V) and antimony (III,V) in water samples by dispersive liquid–liquid micro extraction separation and electrothermal atomic absorption spectrometry (ETAAS) is presented. At pH 1, As(III) and Sb(III) are complexed with ammonium pyrrolidine dithiocarbamate and extracted into the fine droplets formed when mixing carbon tetrachloride (extraction solvent), methanol (disperser solvent) and the sample solution. After extraction, the phases are separated by centrifugation, and As(III) and Sb(III) are determined in the organic phase. As(V) and Sb(V) remain in the aqueous layer. Total inorganic As and Sb are determined after the reduction of the pentavalent forms with sodium thiosulphate. As (V) and Sb(V) are calculated by difference. The detection limits are 0.01 and 0.05 $\mu\text{g L}^{-1}$ for As(III) and Sb(III), respectively, with an enrichment factor of 115. The relative standard deviation is in the 2.9–4.5% range. The procedure has been applied to the speciation of inorganic As and Sb in bottled, tap and sea water samples with satisfactory results.

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1. Introduction

Arsenic and antimony mainly occur in two oxidation states and may form several inorganic and organic species with very different physicochemical properties. Inorganic compounds of As and Sb are more toxic than their organic forms and may be found in ground and surface waters [1]. The toxicity of As(III) and Sb(III) is 10–20 times higher than that of As(V) and Sb(V), and their oxides have been shown to cause several types of cancer [2,3]. To obtain sufficient information on the toxicity and biotransformation of these elements, it is necessary not only to determine the total amount but also to speciate the different oxidation states.

Since the concentrations of these elements in water are very low, sensitive analytical techniques are required, and so inductively coupled plasma mass spectrometry (ICP-MS) [4,5], inductively coupled plasma atomic emission spectrometry (ICP-AES) [6,7], hydride generation atomic absorption spectrometry (HG-AAS) [8,9] and electrothermal atomic absorption spectrometry (ETAAS) [10,11] have been recommended for the purpose. ETAAS appears an attractive option because it is a well-established technique available in practically all laboratories, although due to the very low As and Sb levels usually present in waters, direct determination and speciation is difficult. A number of separation and preconcentration procedures involving hydride generation [12,13], liquid–liquid extraction [14,15], solid phase extraction [16,17] and coprecipitation [18,19] have been proposed to overcome this. However,

the applicability of these procedures is limited by certain disadvantages: they are time-consuming, sometimes provide unsatisfactory enrichment factors, use large volumes of organic solvents and produce secondary wastes. Cloud point extraction [20,21] and liquid-phase micro extraction [22,23] are fairly new methods of sample preparation, which have proved to be simple and inexpensive, opening up interesting ways to deal with the subject.

Recently, a microextraction technique based on a ternary solvent system has been developed. In this technique, termed dispersive liquid–liquid microextraction (DLLME) [24], an appropriate mixture of an extraction solvent and a disperser solvent is rapidly injected into an aqueous sample so that a cloudy solution is formed. The analyte in the sample is then transferred to the fine droplets of the extraction solvent and phase separation is performed by centrifugation. The advantages of this method include its simplicity of operation, rapidity, low cost, low consumption of organic solvents and high enrichment factors. The technique has been applied to the determination of trace organic pollutants and metal ions in environmental samples [25,26] and has recently been revised in depth in the framework of a general review dealing with miniaturized preconcentration methods [27].

The aim of this work is to combine DLLME with ETAAS to develop a new procedure for the determination of trace As and Sb in natural water samples. Ammonium pyrrolidine dithiocarbamate (APDC), a chelating agent which originates stable complexes with a number of metals and has found numerous applications in trace element separation and preconcentration methods [28], is used to extract As (III) and Sb(III) into the organic phase. The fact that As(V) and Sb(V) do not react with APDC allows speciation of the inorganic trivalent and pentavalent forms of these elements.

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