Determination of arsenic in biological fluids by electrothermal atomic absorption spectrometry

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A procedure for the determination of the total content of arsenic in urine, serum and blood by electrothermal atomic absorption spectrometry (ETAAS) is described. Zeeman correction is used to compensate the high background signals. The samples are diluted (1 + 1 for urine and 1 + 3 for both serum and blood samples) in a medium containing 0.1% w/v Triton X-100 before being introduced directly into the furnace. A solution containing 15% w/v hydrogen peroxide, 0.65% w/v nitric acid and 0.5% w/v nickel is also introduced into the atomizer by means of a separate injection. Calibration is carried out against aqueous standards for blood and serum samples and using the standard additions method for urine samples. The detection limit is 20 pg (2 ng ml⁻¹). The reliability of the procedure is checked by analyzing three certified reference materials and by recovery studies.

Introduction

The main route of arsenic uptake is perorally together with food and beverages, by inhalation in factories and smelters, and during the spraying of insecticides. Arsenic is bound to proteins in serum and to the globin part of hemoglobin in erythrocytes; it is stored first in the liver, kidney, spleen and lung. Normal levels in body fluids and tissues are influenced by food to a greater extent than the environment. The daily intake of arsenic with food is estimated as 0.05–0.1 mg, while the total body content of arsenic may be 0.3–4.0 mg. Blood levels of unexposed persons have been reported in the range 0.5–40 µg l⁻¹. Normal urine levels are generally lower than 10 µg l⁻¹ although they may increase up to 80 µg l⁻¹ reaching, after the consumption of seafood, as much as 300 µg l⁻¹;² although it has not been proved that arsenic is an essential element for humans, it is probably so.²

Electrothermal atomic absorption spectrometry (ETAAS) is widely used for trace and ultratrace metal analyses in biological samples because it offers excellent detection limits with minimum sample consumption. Most methods for total arsenic determination require a complete decomposition of all arsenic compounds present in the sample.³ This can be achieved by a number of decomposition procedures, with wet ashing being the most frequently used. However, this procedure is time-consuming and prone to contamination or analyte loss. An alternative is the direct analysis of the biological fluid without the previous mineralization step. In any case, matrix modification is necessary to allow increased pyrolysis temperatures, and thus to decrease the non-specific absorption signals originating from the matrix. Nickel salts⁴–⁶ have been widely used as matrix modifiers for arsenic determination, although other chemicals have also been suggested for the same purpose.⁷–¹¹ In addition, the presence of iron and phosphate in biological matrices causes deuterium arc background correction systems to overcompensate at arsenic resonance lines such as 193.7 and 197.2 nm and so Zeeman-based background correction is commonly recommended.⁹,¹⁰,¹²

Despite the use of this correction procedure, problems in arsenic determination caused by high background levels and the build-up of carbonaceous residues inside the atomizer still remain, drawbacks which can be avoided by including an oxygen or air–pyrolysis step in the heating cycle.¹³,¹⁴ However, this option is not possible for all the commercial electrothermal atomizers and involves a risk of decreasing the useful lifetime of the expensive pyrolytic material. Recently, it has been demonstrated that the addition of both hydrogen peroxide and nitric acid to samples of a high organic content can also alleviate these problems; an additional advantage being that no damage is produced in the graphite atomizers.¹⁵,¹⁷ This is a simple way of producing an oxidizing environment inside the atomizer and effective in situ mineralization of the sample.

In this study, a procedure based on such a simple strategy for the determination of total arsenic in human urine, serum and blood is discussed. The samples are simply diluted in a medium containing Triton X-100 and directly introduced into the electrothermal atomizer. A second aliquot containing hydrogen peroxide, nitric acid and a nickel salt is then injected, which allows reduced background signals to be obtained.

Experimental

Apparatus

An ATI-Unicam (Unicam Atomic Absorption, Cambridge, UK) 939QZ atomic absorption spectrometer equipped with a GF90 electrothermal atomizer and a FS90 Plus autosampler were used. Zeeman correction was used to obtain the background-corrected integrated absorbance, which acted as the analytical signal. Pyrolytic platforms (reference 9423 393 95191) were obtained from ATI-Unicam. Argon was used as the inert gas, the flow rate being 300 ml min⁻¹ during all the stages except atomization, when the flow was stopped. Measurements were performed, with a spectral bandwidth of 1.0 nm at 193.7 nm using a hollow cathode lamp (Photon PTY. LTD., Australia) operated at 8 mA.

Reagents

All the chemicals used were of the highest purity available and all the glassware and plasticware was nitric acid-washed and rinsed with ultrapure water. High quality water, obtained using