

Determination of Arsenic (III) and Arsenic (V) in Natural Waters by Cathodic Stripping Voltammetry at a Hanging Mercury Drop Electrode

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The presence of arsenic in natural water is of concern because of its toxicity and possible carcinogenic activity, and the biological effects of arsenic are significantly altered by its oxidation state as well as complexation with organic materials [1]. Depending on the environment, arsenic can exist in the two different oxidation states As (III) and As (V) in natural water, although As (V) is thermodynamically favoured. Because of its ability to complex with certain co-enzymes, As (III) is more toxic to animal and plants than As (V). Therefore, the speciation of arsenic species is important to understand for both the biological as well as the geochemical behaviour of this element. The ratio As(III)/As(V) may be an indicator of the time of the percolation of the water in the underground as well as of the deep it had circulated and the assessment of infiltration of rainwater in the circulation channels.

The methods employed so far for the determination of trace amounts of arsenic are some spectral methods and radioactive ones but recently electrochemical techniques especially stripping voltammetry have been used, too [2]. As (III) can be reduced to the element in acidic solution and deposited onto a solid electrode such as gold, platinum or copper, and then stripped using anodic stripping voltammetry. However, there are often problems associated with ASV at solid electrodes such as 'memory' effects, limited sensitivity, and poor precision which make them inconvenient for routine analysis. In an attempt to avoid these problems, cathodic stripping voltammetry at a hanging mercury drop electrode (HMDE) has been used to determine arsenic, involving the reaction between arsenic and copper or selenium to form an intermetallic compound that can be pre-concentrated on the HMDE and then stripped cathodically [3].

In this work arsenic (III) and arsenic (V) are determined in natural waters by cathodic stripping voltammetry using a HMDE. The method requires the presence of copper (II), as it involves a pre-concentration step of a copper-arsenic intermetallic compound at the mercury electrode. Generally, the methods proposed for the determination of both arsenic (III) and arsenic (V) consists on the determination of the first compound, followed by reduction of arsenic (V) to arsenic (III), and determination of total arsenic; arsenic (V) is obtained by difference. The problem is that, although several methods have been proposed for the reduction [2, 4, 5], none of them was able to produce acceptable results. In this work a new method is proposed, involving the reduction of arsenic (V) with thiosulfate and the subsequent determination of the arsenic (III) formed; due to the presence of the reductant, the voltammetric conditions for the determination of arsenic (III) had to be modified, with a much higher amount of copper ion being required for the formation of the copper-arsenic intermetallic compound. The method is simple, with no need for the elimination of the excess of reductant, and proved to be reliable.

Detection limits of 0.4 ppb for arsenic (III) and of 2 ppb for arsenic (V) were obtained in simple water solutions. No interference was observed for a great number of ions: Ca²⁺, Mg²⁺, Ba²⁺, Na⁺, K⁺, Li⁺, Si⁴⁺, Fe²⁺, Mn²⁺, Sr²⁺, NH⁴⁺, SO₄²⁻, F⁻, Cl⁻, Br⁻, PO₄³⁻, HCO₃⁻, Be²⁺, Cr³⁺, Co²⁺, Al³⁺, Ge⁴⁺, Pb²⁺, Sn⁴⁺. Severe interference was observed for the ions Se⁴⁺, Bi³⁺, Sb³⁺, S²⁻. Interference of Cd²⁺, Fe³⁺, Zn²⁺, NO₂⁻ and NO₃⁻ is important too, but only for concentrations that are not expected in spring and mineral waters. The method was used in the determination of arsenic (III) and arsenic (V) in several spring and mineral waters and the value for total arsenic correlated well with that obtained by EE-ICP with hydride generation.

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