

Comparison of some reaction media for the determination of arsenites by hydride generation atomic absorption spectrometry

Ingrid Hagarová¹, Peter Matúš¹, Jana Kubová¹, Marek Bujdoš¹, Pavel Diviš²

¹Comenius University in Bratislava, Faculty of Natural Sciences, Mlynská dolina 1, 842 15 Bratislava, Slovakia, e-mail: matus@fns.uniba.sk

²Brno University of Technology, Faculty of Chemistry, Purkyňova 118, Královo Pole, 612 00 Brno, Czech Republic

In waters, arsenic is generally found in the inorganic forms of arsenite (As(III)) and arsenate (As(V)). The As(V) forms predominate in oxygenated waters while in deep well waters, where reducing conditions exist, the trivalent species may be present. Because these inorganic species show different toxicity, mobility, and behaviour in biological systems, their differentiation has generated considerable interest.

Many methodologies exist for the speciation analysis of As in water samples. Selective reduction procedure based on the highly pH-dependent reaction between arsenic species and NaBH₄ to generate arsine in hydride generation atomic absorption spectrometry (HG AAS) system is relatively commonly used. In this case, for As(V) strongly acidic solution is required (pH ≤ 1), while for As(III) hydride formation occurs in mildly acidic solutions (1).

The reaction between NaBH₄ and arsenic in solution is sensitive to pH and it appears that, for the reaction to proceed rapidly, the target species must not be present in solution as a negatively charged species. This means that arsenates must be fully protonated if they have to be converted to arsines. As pK₁ for arsenic acid is 2.3, the reaction must therefore be carried out at very low pH (1-2 mol l⁻¹ HCl is commonly employed). Arsenites, on the other hand, are protonated under most conditions (pK₁ = 9.2) and will react with NaBH₄ under conditions which are only mildly acidic. In the absence of other arsenic species, differentiation of arsenate and arsenite can therefore be simply achieved by exploiting the pH dependency of the NaBH₄ reaction with As.

The aim of this study was to critically evaluate the most frequently used reaction media for the speciation analysis of arsenite in the presence of arsenate. Four different reaction media has been used to achieve a selective volatilization of arsenite: 1.5 mol l⁻¹ HCl (pH <1.0), 0.1 mol l⁻¹ acetic acid (pH ~2.9), citrate buffer (pH ~3.1), acetate buffer (pH ~5.0) and phosphate buffer (pH ~7.2).

All the studied reaction media can be used for the selective volatilization of As(III) but the serious problem caused by the interference of As(V) was observed (in 0.1 M acetic acid, citrate buffer and acetate buffer) when relative content of As(III) was less than 10 % (from all the present arsenic). Natural waters usually contain less than 10 % of As(III), so speciation in the real samples should be accompanied with another speciation analysis procedure to confirm the accuracy of obtained data. This problem was not observed in phosphate buffer but in this case the sensitivity was significantly lower and the speciation analysis in this medium can be done only if relatively high contents of As(III) in the samples are present.

Reference

1. I. Hagarová, Chem. Listy 101 (2007) 768-775.

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