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Publisher Taylor & Francis

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International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

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To cite this Article Starv, J. , Zeman, A. , Kratzer, K. and Praslova, J.(1980) 'Radioanalytical Determination of Arsenic(III) and (V) in Natural Waters', International Journal of Environmental Analytical Chemistry, 8: 1, 49 – 53

To link to this Article: DOI: 10.1080/03067318008071878

URL: <http://dx.doi.org/10.1080/03067318008071878>

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Radioanalytical Determination of Arsenic(III) and (V) in Natural Waters

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(Received December 11, 1979)

The previously described radioanalytical method for the determination of arsenic has been adapted to the analysis of natural waters. The preconcentration using diethyldithiocarbamate extraction increases the sensitivity of the method up to 0.2 ppb. The procedure is highly selective: none of 34 metals and 9 anions tested interfere in the determination even if present in a great excess. The results of the analysis of tap, river and mineral waters showed that arsenic is present predominantly in the pentavalent state.

KEY WORDS: Radioanalytical method, traces of arsenic(III) and (V), natural waters, diethyldithiocarbamate extraction.

INTRODUCTION

The previously described radioanalytical method¹ is based on the extraction of arsenic(V) in the presence of tungstate, labelled with tungsten-185, and an excess of molybdate into tetraphenylarsonium chloride in 1,2-dichloroethane. Only the tungstomolybdoarsenic heteropolyacid is extracted into the organic phase (but not the molybdotungstic acid). The activity of the organic phase is proportional to the amount of arsenic(V) in the sample. Phosphorus(V) reacts similarly and thus interferes in the determination. The interference caused by cations and anions forming precipitates or complexes with arsenic(V), molybdenum(VI) and tungsten(VI) can also be expected.

The purpose of the present work is to develop a suitable preconcentration method which increases both the selectivity and sensitivity of the method for its use in the analysis of natural waters.

EXPERIMENTAL

Reagents and apparatus

All reagents used, unless otherwise stated, were of A.R. or suprapure quality.

The solution (0.01 M) of diethylammonium salt of diethyldithiocarbamate (DDDC) was prepared by dissolving 1.11 g of the reagent in 500 ml of redistilled chloroform or carbon tetrachloride.

Potassium iodide solution (5 M) was prepared by dissolving 207.1 g of the reagent in 500 ml of tridistilled water to which 1 g of ascorbic acid was added. Thus prepared solution was purified before each set of experiments by shaking with the same volume of 0.01 M DDDC in chloroform.

A 0.15 M solution of sodium nitrite was prepared by dissolving 7.2 g of the reagent in 500 ml of tridistilled water.

The solution of ammonium molybdate was obtained by the dissolution of 8.825 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ in 500 ml of tridistilled water.

A 0.01 M solution of tetraphenylarsonium chloride (Ph_4AsCl) was prepared by dissolving 2.184 g of $\text{Ph}_4\text{AsCl}\cdot\text{H}_2\text{O}$ in 500 ml of 1,2-dichloroethane.

^{74}As (Amersham, England) in the form of arsenic acid in 0.4 M hydrochloric acid was diluted with water to the appropriate concentration.

^{185}W (Swierk, Poland) in the form of sodium tungstate in 0.3 M sodium hydroxide was diluted 200–1000 times with 0.001 M sodium hydroxide.

The radioactivity was measured using a well-type NaI(Tl) crystal (for counting of ^{74}As) and a plastic scintillation detector (for counting ^{185}W).

Development of the method

For the separation and preconcentration of arsenic(III) the extraction method² using 0.01 M DDDC in carbon tetrachloride was studied using ^{74}As . It has been found that during 2 min shaking arsenic(III) can be completely (>98–99%) extracted from 250 ml sample of tap, river or mineral waters, which are 1 M in hydrochloric acid, into 25 ml of 0.01 M DDDC in carbon tetrachloride. Under these conditions arsenic(V) remains entirely in the aqueous phase. For the quantitative reduction of arsenic(V) into the trivalent state heating with the excess of potassium iodide is necessary. Arsenic(III) can be completely transferred from the organic phase into a mixture of 2.0 ml of nitric acid (1:3) and 3.0 ml of 0.15 M sodium nitrite. During 2 min shaking, arsenic(III) is completely oxidized to the pentavalent state.

Determination of arsenic(III)

25 ml of conc. hydrochloric acid and 25 ml of 0.01 M DDDC in carbon tetrachloride were added to the 250 ml aqueous sample in a 500 ml separation vessel. The mixture was shaken for 2 min and a 20 ml aliquot of the organic phase was shaken for another 2 min with a mixture of 2.0 ml of nitric acid (1:3) and 3.0 ml of 0.15 M sodium nitrite. To 4.0 ml of the separated aqueous phase, 1.0 ml of sodium tungstate-185 and 1.0 ml of ammonium molybdate solution were added and the mixture was shaken for 4 min with 2.0 ml of 0.01 M Ph_4AsCl in 1,2-dichloroethane. 0.3 ml of the organic extract was pipetted on an aluminium disc and evaporated to dryness. As a blanc, 250 ml of tridistilled water, treated as described above, was used. For the determination of the content of arsenic(III) both the calibration curve and the standard addition method were used.

Determination of total arsenic

25 ml of conc. hydrochloric acid and 5 ml of 5 M KI were added to 250 ml of the aqueous sample and the mixture was heated to boiling. After cooling to room temperature, 25 ml of 0.01 M DDDC in carbon tetrachloride were added and the mixture was treated as described above. The content of arsenic(V) was calculated from the difference between total arsenic and arsenic(III). Arsenic(V) can also be determined directly after the separation of arsenic(III) by DDDC extraction.

Effect of foreign metals and anions

The above described procedure was tested for the determination of arsenic(V) in the presence of a hundredth-fold excess of foreign metal cations and anions. From the results, presented in Table I, it is evident that none of 34 metals and 9 anions tested interfere in the determination.

RESULTS AND DISCUSSION

The tap water of the city of Prague (Water plant, Podolí) was analysed for the content of arsenic during 1979. It contained from 0.7 to 1.0 ppb of arsenic (mean value 0.8 ± 0.1 ppb) predominantly in the pentavalent state. The amount of arsenic(III) was under the detection limit (< 0.2 ppb). These results are in an agreement with experiments in which $^{74}\text{As(III)}$ and $^{74}\text{As(V)}$ were added to the tap water: arsenic(III) was oxidized to the pentavalent state within several hours by chlorine present in the tap water.

Vltava-river water, which is used for the production of potable water,

TABLE I

Determination of 6.25 µg of arsenic(V) in 250 ml sample (25 ppb) in the presence of a hundred-fold excess of foreign metals and anions

Metals or anions present	Arsenic found (µg)	Yield (%)
Be	6.03	96.5
Mg	6.57	105.2
Ca, Sr	6.40	102.1
Ba	6.50	104.1
Be, Mg, Ca, Sr, Ba	5.75	92.0
Cu, Ag, Zn, Cd, Hg	6.50	104.1
B, Al, Ga, In, Tl(I), La, Eu	6.08	97.3
Si, Ge, Sn(II), Pb	6.06	97.0
Ti(III), Zr, Th	6.18	98.9
Sb(III), Bi	6.16	98.6
V(V), Ta, Se(IV), Te(IV)	6.26	100.2
Cr(III), Cr(VI), Mo(VI), W(VI), U(VI)	6.28	100.5
F ⁻ , Br ⁻ , CNS ⁻ , SO ₄ ²⁻ , PO ₄ ³⁻	6.48	103.7
HCO ₃ ⁻ , SO ₃ ²⁻ , H ₂ S, CH ₃ COO ⁻	6.11	97.8

contained from 1.9 to 3.0 ppb of total arsenic (mean value 2.4 ± 0.4 ppb). In this case, however, 0.3–0.5 ppb of arsenic(III) has been detected. The addition of arsenic(III) and arsenic(V), labelled with ⁷⁴As, showed that both forms are rather stable in Vltava-river water: the oxidation of arsenic(III) was observed only after several days. Our results can be compared with those concerning the arsenic content in Japanese rivers (0–34 ppb of arsenic(V), 0–4 ppb of arsenic(III))³, USA rivers (1.1–42 ppb of arsenic(V), 0.04–6.5 ppb of arsenic(III))^{4,5} or Swiss rivers (0.4–2.8 ppb of total arsenic)⁶.

Great differences in the content of arsenic have been found in various bottled mineral waters commercially available in the ČSSR. The highest content has been found in Ida mineral water (Běloves): 227 ± 7 ppb of arsenic(V) and 2.4 ± 0.2 ppb of arsenic(III); because of the high content of arsenic(V), the samples had to be diluted before the analysis 10–25 times with tridistilled water. On the other hand, Rudolf (Mariánské Lázně source) and Šaratica (Sokolnica source) contain 0.6 ± 0.1 ppb of arsenic(V) (arsenic(III) was not detected) and Ondráš (Moravský Beroun source) contains only 0.4 ± 0.1 ppb of arsenic(V) (arsenic(III) was not detected).

Acknowledgement

The authors wish to express their thanks to Mrs. T. Vrbská for her technical help.

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