

A FIELD METHOD OF SPECTROPHOTOMETRIC DETERMINATION OF ARSENIC IN WATER INCLUDING A SPECIATION

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1. Introduction

Inorganic forms of arsenic appear as As (III) and As (V). As to organic species, monomethylarsonate (MMA) and dimethylarsinate (DMA) are especially important. A survey regarding natural abundance of As - species is described by Dunemann and Begerow [1].

The behaviour of arsenic in aquatic systems depends on the pH value, redox potential and bioalkylation. By the EPA it was stated that arsenic in groundwater predominantly occurs as As (V) [2]. Korte and Fernando [3] suppose that the part of As (V) was overestimated in former time because of errors of sampling, sample preservation, and chemical analysis.

There are contradictory views regarding stability of As (III) in water samples as reviewed in the papers e.g. [4, 5]. Generally, it cannot be supposed that the oxidation of As (III) to As (V) is a slow process. Therefore, in situ determination of arsenic is favourable.

For this reason, a method was developed to determine total arsenic as well as the species As (III) and As (V) by field measurement.

2. Method survey

The quantitative determination of arsenic in water is dominated by methods involving arsine generation. In this connection, the separation of analyte and matrix is an advantage. This method is applied in hydride generation atomic absorption spectrometry (HGAAS) and also in spectrophotometry using silver diethyldithiocarbamate reagent.

By HGAAS, a speciation regarding As (III) and As (V) is possible [6]; The arsine generation is a fast process and therefore there are differences between As (III) and As (V).

Chromatographic methods hyphenated with spectrometric determination are predestined for speciation. Examples are the coupling of GC or HPLC with ICP / MS and HGAAS, respectively [7 - 10].

Furthermore, Grabinski described an off-line coupling of ion-exchange separation and GFAAS detection for the determination of As (III), As (V), MMA and DMA [11].

Spectrometric methods require a high instrumental expense and, therefore, they are not favourable for site analysis.

On principle, spectrophotometry is suitable for field analysis. The method is well-suited for laboratory use of the determination of total arsenic, e.g. DIN EN 26595 [12]. However, in contradiction to the HGAAS, a speciation is more difficult because the arsine generation (using metal and acid) must be of moderate velocity.

In this paper, an instrumental and methodical adaption of the spectrophotometric laboratory process is described, fulfilling the conditions of the field analysis including speciation.

Additionally, attempts were made to apply the ion-exchange method as described by Grabinski [11] for the separation of inorganic species.

3. Experimental part

The usual method of arsine generation using tin chloride, potassium iodide, zinc, copper sulphate, and sulphuric acid was applied.

For the absorption of arsine and the dye formation the current reagent solution containing 0.5 % silver diethyldithiocarbamate in pyridine was used [12].

3.1. APPARATUS

A precondition for the spectrophotometric field measurement is that the procedure (arsine generation, passing-in, and absorption) is carried out in a simple way using small-scale equipment and that a transportable spectrophotometer is available (e.g. DR 2000; HACH Comp., USA).

Therefore, arsine generation was carried out in a 40-ml EPA vial, closed by septum and a screw cap. The arsine was passed through a small plastic tube, connected with this septum and at the other end with a pipette tip containing a lead acetate wad. The pipette tip dipped in the 1-cm cuvet of the spectrophotometer filled with reagent solution.

Generation vial and cuvet were kept in holes of a special block of plastic material. This block can hold 5 generation devices, thus enabling several samples to be treated simultaneously.

3.2. ANALYSIS CONDITIONS

The EPA vial was filled with 20 mL of the water sample or of the calibration solution and subsequently solutions of the reduction substances were added.

The concentrations of these solutions correspond to those described in the DIN EN 26595 [12]. The amounts to be added were modified in order to obtain concentrations (relative to the total volume) comparable to those of the DIN standard.

In contradiction to the usual practice, tin chloride and sulphuric acid were added as a mixture („reducing solution “).

After closing the EPA vial, the arsine generation was induced by injecting 2 mL of the reducing solution through the septum. After about 30 min reaction time, 2 mL reduction solution was injected again (not for speciation). (The injection of solutions to carry out the chemical reactions on a small scale is described by Roesky and Kusche [13].)

After the arsine generation was finished, the cuvet was measured at a wavelength of 525 nm against a blank. For more detailed information regarding the conditions of analysis see [14].

3.3. METHOD DEVELOPMENT

3.3.1. Volume of the reagent solution

The direct passing-in of arsine into the reagent solution in the cuvet leads to the question, whether the absorption is quantitative, more exactly, whether the minimum value of reagent solution necessary for quantitative absorption is within a volume range, given by the smallest value (1.5 mL) fixed by the beam of light of the spectrophotometer (and by the vaporization of pyridine), and by the largest value (2.1 mL) in consequence of the increasing possibility of reagent solution overflow.

It was shown by tests, that the absorption of arsine is quantitative in this volume range, independently of the volume of reagent solution. To be sure that the measuring procedure is correct on the one hand, and to get a small detection limit on the other, a volume of 1.7 mL was used for the routine analysis.

3.3.2. Optimization of reduction condition

Experiments regarding time dependence of arsine development using both As (III) and As (V) solutions were carried out to study the action of reduction substances and likewise to optimize analytical conditions.

The following results were obtained:

- Tin chloride is the essential agent for the reduction process. A concentration of 4 mg/L (in the total solution) was sufficient.
- For the determination of total arsenic it is necessary to add tin chloride and potassium iodide as well as copper sulphate. There was a high reduction rate and the arsine development was finished within 45 min. After this period there was no difference between As (III) and As (V).
- Potassium iodide promotes the arsine generation only in the case of the presence of tin chloride. Therefore, it predominantly acts as a catalyst for the acidity available.
- Carrying out the reduction process without potassium iodide, a significant difference results between As (III) and As (V). The maximum of the absorbance difference was reached at 15 min, independently of the concentration of arsenic. Hence, a speciation between As (III) and As (V) is possible.
- In the absence of copper sulphate there is a lack of local elements and, as a consequence, the amount of arsine was to small.

3.3.3. Determination of total arsenic

The method was calibrated regarding the second section of paragraph 3.3.2. and reproducibility and detection limit were calculated.

There was no difference between the calibration functions of As (III) and As (V). The curves were linear up to 500 $\mu\text{g/L}$ As. Above this concentration, the absorbances varied and increased after the end of the passing-in process. This fact may be interpreted in such a way that the dye development is not finished yet.

Using the results of calibration, the following relative confidence intervals were calculated (level of significance $P = 95 \%$):

$$\text{As (III) : } c = \pm 6 \%$$

$$\text{As (V) : } c = \pm 8 \%$$

The higher value of As (V) as compared to As (III) may be explained by the additional reduction step.

A detection limit (3 s Ö 2 - criterion) of 5 µg/L was obtained for the total arsenic concentration.

3.3.4. Speciation

As mentioned above, a speciation of As (III) and As (V) is possible, if the reduction is carried out without potassium iodide and if the arsine passing-in is stopped after 15 min. Calibrations were carried out for both As (III) and As (V) and the following regression functions were obtained:

$$\text{As (III) : } c = 1.24 + 464 * E \quad (1)$$

$$\text{As (V) : } c = 1.06 + 815 * E \quad (2)$$

c = concentration

E = absorbance

The reciprocal of the slope (absorption coefficient) was nearly twice as large as in case of As (III). Therefore, a speciation is possible with a sufficient accuracy.

The calculation is carried out using the following equations:

$$C_{\text{As(III)}} = \frac{E_{\text{Spec}} - \epsilon_{\text{As(III)}} \cdot C_{\text{ges}}}{\epsilon_{\text{As(III)}} - \epsilon_{\text{As(V)}}} \quad (3)$$

$$C_{\text{As(V)}} = C_{\text{ges}} - C_{\text{As(III)}} \quad (4)$$

E_{Spec} = absorbance in the speciation

c_{ges} = concentration of total arsenic

ϵ = absorption coefficients in the speciation calibrations

In equation (3) all the quantities have an error. Therefore, regarding the law of accumulation of errors the reproducibility becomes worse. The relative confidence interval for the determination of As(III) amounts to $\pm 17 \%$ (double determination; P = 95 %).

A principal possibility of in-situ speciation consists in the use of the ion-exchange method, mentioned above [11]. Using this method, the separation of As (III) and As (V) is based on the difference of the first dissociation constants of their corresponding acids (pK = 9.2 and 2.26, respectively [11]).

First experiments were carried out with an anion exchanger (Wofatit AD 41; column: 12 * 0.6 cm) and according to Grabinski [11] 0.006 M trichloroacetic acid was use as eluent. The separation of As (III) (eluate) and As (V) (remains on the resin) was confirmed.

A disadvantage of this method is the dilution of the feed volume by the eluent (peak broadening) and therefore the increase in the detection limit.

For instance, if 4 mL of feed volume was used to obtain 20 mL of analytical volume, the detection limit increased by a factor of 5. Furthermore, the separation is an additional source of error and the recovery only amounts to about 80 - 90 %. Thus the detection limit may be 30 - 40 µg/L.

4. References

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