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Preservation of arsenic species in water samples using phosphoric acid – Limitations and long-term stability

B. Daus*, H. Weiss, J. Mattusch, R. Wennrich

UFZ Centre for Environmental Research, Permoserstrasse 15, 04318 Leipzig, Germany

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Abstract

The preservation of arsenic species in water samples is an indispensable method to avoid their changes during storage, if it is not possible to analyse them immediately. The aim of this investigation was to demonstrate the limitations of the suggested method by using phosphoric acid as a preservation agent. The samples remain stable for 3 months, even if they show evidence of high concentrations of iron or manganese. Critical is an increasing pH > 3. Theoretically, a precipitation of strengite ($Fe_3(PO_4)_2$) could occur, which should be avoided. Phosphoric acid with a final concentration of 10 mM is recommended as a preservation agent, combined with keeping the samples cool (6 °C) and dark. Filtration of samples before preservation may be carried out with respect to the analytical aim to distinguish between the total and soluble fraction (without colloids). It was shown that filtered and non-filtered samples can be preserved by utilising the above mentioned scheme.
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Keywords: Preservation; Arsenic species; Speciation analysis

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1. Introduction

Arsenic is a widespread contaminant of surface and ground waters. Analytical techniques for determining arsenic species in aqueous samples have been developed several times in recent years [1–5] and have entered into routine analysis.

Always an important consideration in analysis and especially in speciation analysis is the preservation of chemical compounds in the sample from the onset of sampling until the time of analysis. Arsenic is well-known to exist in two oxidation states (arsenite and arsenate) in water samples which can easily change. With regard to preservation of the species in their original state when sampling takes place, the influencing factors of the two arsenic species on the redox-reaction have to be discussed. The following points have to be considered: (1) redox potential, (2) redox couples, (3) precipitation/sorption, (4) microbial activity, (5) light, and (6) temperature.

Theoretically, the redox potential together with the pH value determines the ratio between the two arsenic species. However, it has been shown that arsenic species are often not in equilibrium due to kinetic effects [6]. Additionally, preservation of the redox condition of a water sample may be difficult due to problems in measuring the correct redox potential [7] and the difficulties in using suitable redox buffers for a certain redox value.

A second strategy consists of the removal or complexation of potential redox counterparts without influencing the equilibrium between the different arsenic species. It has been shown before [6] that oxygen alone, originating from air, is not able to oxidize arsenite. The presence of an additional redox counterpart seems to be necessary [6] to mediate the reactions. Dissolved or colloidal iron or manganese compounds are common redox counterparts in natural waters. Consequently, the exclusion of these counterparts from the reaction could be a possible method for successful preservation by means of complexation [8–10].

Precipitation of interfering components is an obvious feature in the reduction of element concentrations in water samples; however, in addition to the formation of quasi-soluble compounds of some water constituents, a co-precipitation and sorption of the element concerned may take place. Well-known in this context is the sorption of arsenic on amorphous iron hydroxides but it may also occur for other precipitates. A prevention of all precipitation processes is imperative for species preservation.

Light and temperature are additional factors, which have to be considered. The influence of light on the oxidation of arsenite

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* Corresponding author. Tel.: +49 341 2352058; fax: +49 341 2352126.
E-mail address: birgit.daus@ufz.de (B. Daus).

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Table 1
Solubility constants of relevant phosphates

Mineral	Vivianite $Fe_3(PO_4)_2{\cdot}8H_2O$	Strengite $Fe_3(PO_4)_2$	$Mn_3(PO_4)_2$	$MnHPO_4$	Hydroxyapatite $Ca_5(PO_4)_3OH$
$\log K_s$	−36	−26.4	−23.827	−12.947	−3.421

was shown to be important [10–12]. Therefore, keeping the water samples in the dark is advisable. Temperature has influence on microbial activity as well as on chemical reactions (endothermic/exothermic). Cooling the water samples in a fridge (∼6 °C) was shown to be the best method for preservation of arsenic species [10,13].

Several methods for preservation of arsenic redox species were suggested in recent publications [5,8,10,14,15], most of them based on acidification (e.g. HCl) of the water sample or application of strong complexing agents (e.g. EDTA). Generally, a preservation agent has to fulfil the intended task with a minimum of undesired effects on the sample. This paper focuses on the addition of phosphoric acid for preservation of arsenic species in water samples as described before [10] with special focus on possible limitations of the method.

The formation of phosphate precipitates may occur when preserving water samples with phosphoric acid. Relevant and well known phosphates in natural water samples are the iron phosphates (strengite $Fe_3(PO_4)_2$; vivianite, $Fe_3(PO_4)_2{\cdot}8H_2O$), calcium phosphates or manganese phosphates. Table 1 summarises the solubility constants of the relevant phosphates from the database WATEQ4f.dat (proved database of PHREEQC computer program [16]). The calcium phosphates are not of importance because they are soluble in acid solutions. The iron and manganese phosphates are much more important due to their occurrence in high concentrations in natural waters and their insolubility in acids.

The aim of these investigations was to examine possible precipitation reactions by means of laboratory experiments as well as theoretical calculations. Long-term stability, another important parameter of limitation for such a sample preparation method was tested for field samples containing high concentrations of iron and manganese (up to 8 mg L^{-1}).

2. Experimental

2.1. All chemicals were of analytical grade

2.1.1. Field sampling and sample preservation

Water samples were taken from a seepage water source of abandoned tin mill tailings Bielatal, located south of Saxony in Germany [17,18]. A volume of about 250 mL water was filtered through a membrane filter (0.45 µm, cellulose acetate, Satorius AG, Goettingen, Germany) and divided into sub-samples (100 mL each). One series of samples was acidified with 1 mL of 1 mol L^{-1} phosphoric acid (diluted from concentrated H_3PO_4, 85%, v/v, MERCK, Darmstadt, Germany). A second series remained free of additives. All samples were stored in a cooling box in the field and in a fridge in the lab (6 °C). The samples were measured within 24 h and again after 2 weeks, 3 weeks and 3 months.

The physico–chemical properties as Eh (corrected with the reference electrode potential: 0.220 V), pH, temperature and oxygen contents of the water samples were measured on site.

2.1.2. Lab experiments for testing the influence of iron and manganese concentrations

Solutions with different iron concentrations (0, 10, 20, 40 and 100 mg L^{-1} Fe) prepared from $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ (MERCK) and each one with 100 µg L^{-1} arsenite (diluted from a 0.05 mol L^{-1} aqueous standard solution of $NaAsO_2$, MERCK) were stabilised with a final concentration of 0.01 mol L^{-1} H_3PO_4 (1 mL of a 1 mol L^{-1} H_3PO_4 to 100 mL, see above). The solutions (50 mL each and three replicates for each iron concentration) were stored in a fridge (6 °C, dark) and the arsenic species were measured immediately and after 7, 14 and 21 days. The same procedure was repeated with different concentrations of manganese (0, 10, 20, 40 and 100 mg L^{-1} as $MnCl_2$, MERCK).

2.1.3. Theoretical calculations

The species calculations were carried out by using the geo–chemical computer program PHREEQC [16] and the database WATEQ4f.dat containing the data for the arsenic species. The initial solutions had the same constituents as the lab experiments ($(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ or $MnCl_2 + HAsO_2 + H_3PO_4$). The change of pH was realised through dissolution of $CaCO_3$ as a solid phase.

2.1.4. Analytical methods

The coupling of ion chromatographic separation (BECKMAN, System Gold, Fullerton, USA) and inductively coupled plasma mass spectrometric (ICP–MS) detection (PQ ExCell, THERMO) employing a Meinhard nebulizer was used for the determination of As(III) and As(V). IonPac AG7/AS7 anion exchange columns (DIONEX, Sunnyvale, USA) were used together with a gradient of eluents consisting of 0.4 mmol L^{-1} (eluent A) and 50 mmol L^{-1} nitric acid (eluent B) for the separation of arsenic species. A given method [3] was optimised for a short analysis time for just the two inorganic arsenic species. The final gradient program consisted of five steps (0.3 min 100% A, 0.5 min 100% A–100% B in a linear mode, 0.5 min 100% B, 0.5 min 100% B–100% A in a linear mode and finally 100% A for 3.2 min). The peaks were integrated after baseline correction using the computer program Microcal^{TM} Origin^{TM} (Version 4.10, Microcal Software Inc.). The limit of detection is 2 µg L^{-1} (3σ method).

To determine the total concentrations of As, Fe, Mn, Ca, Mg, and K, ICP–atomic emission spectrometry (ICP–AES) was used. ICP–AES measurements (CIROS, Spectro A.I.) were performed using cross-flow nebulization. Calibration was carried out using diluted ICP multi-element standard solution IV (CertiPUR, MERCK) as well as arsenic single-element standard solutions (MERCK). The linear range was found to be between a few μg L^{-1} and 10 mg L^{-1}.

The anions (SO_4^{2-}, Cl^-, NO_3^-) were determined by using an ion chromatographic device (DX 500, Dionex) with an IonPac AS12A/AG12A column and a conductivity detector. Details about these methods are given elsewhere [19].

3. Results and discussion

Precipitation of strengite and $MnHPO_4$ are most likely (see its low solubility constant (K_s values) in Table 1) in water samples. The critical manganese activity for the formation of $MnHPO_4$ in a pure solution can be estimated simply from the solubility constant and its equation. This means just a rough estimation for natural samples, because only a single equilibrium is considered. The saturation is reached at a manganese concentration of 9.5×10^{-9} mol L^{-1} (71 μg L^{-1}).

Calculation of the iron phosphates, even in pure solutions, is more complicated due to the Fe^{2+}/Fe^{3+} ratio as dependent on the pH and Eh values. The saturation index (SI) may be used for the calculation of possible precipitation. The SI of a phase is defined as

$$SI = \log\left(\frac{IAP}{K_S}\right) \qquad (1)$$

where IAP means the product of ionic activities of the phase components and K_s is its solubility constant. A SI > 0 indicates precipitation of the phase calculated. The calculated SI of strengite as dependent on total Fe concentration is given in Fig. 1 for pH 2 (as 10 mmol L^{-1} H_3PO_4) and two different Eh values using the computer program PHREEQC. The SI is always negative for the high Eh value of 236 mV (equivalent to pe = 4) and only near 0 for the Eh of 473 mV (equivalent to pe = 8) and a very high iron concentration. Usual iron concentrations (up to 100 mg L^{-1}) are tolerable with respect to the forming of precipitates within this wide Eh window.

Another relevant factor is the pH value. Due to the Fe^{2+}/Fe^{3+} equilibrium, the SI of strengite increases with higher pH (see Fig. 2). Besides the precipitation of phosphates, the forming of quasi-soluble iron hydroxides has to be considered. Fig. 2 shows, as an example, the SI of hematite (log K_s = −30.845). It is obvious that the pH should be 2 or less in order to avoid precipitation. This is in accordance with sampling procedures, which are generally described in the sampling of water and the subsequent determination of trace elements, for example [20]. It is not as critical for samples with higher redox potential as shown for Eh = 478 mV. However, samples with low Eh values and higher proportions of arsenite are of more interest with respect to preservation of this species.

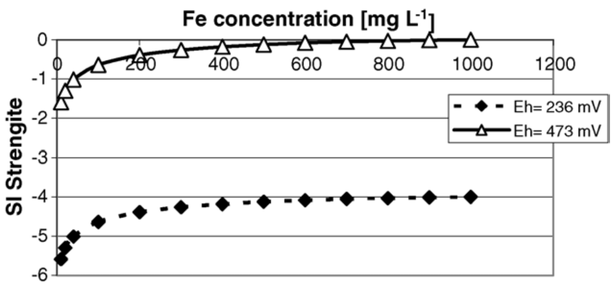

Fig. 1. Saturation index (SI) of stengite as dependent on Fe concentration and on Eh value, 0.01 mol L^{-1} H_3PO_4, pH 2.

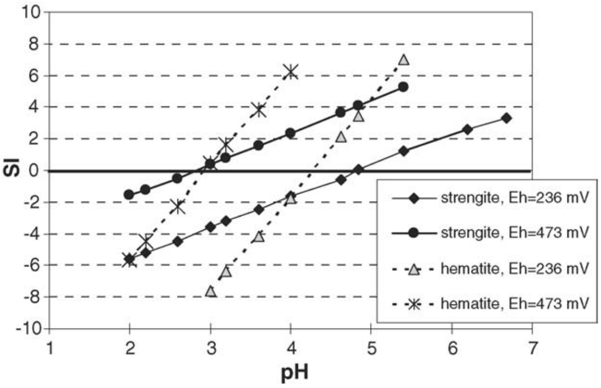

Fig. 2. Saturation index (SI) of strengite and hematite as dependent on pH, 10 mg L^{-1} Fe as $(NH_4)Fe(SO_4)_2{\cdot}2H_2O$, 100 μg L^{-1} arsenite and 0.01 mol L^{-1} H_3PO_4.

Such theoretical results based on idealised equilibrium conditions indicate that no precipitation may occur if the pH ≤ 2 and the iron concentrations are roughly <100 mg L^{-1}. Samples with higher iron concentrations, which are typical, e.g. for acid mine drainage waters [21–23], could represent a special case, also with respect to ion chromatographic separation, whereby such high iron concentrations could disturb the separation and cause memory effects. A speciation of arsenic in such samples could, in any case, be difficult for this reason applying hyphenated techniques. Consequently, the preservation method is focused on samples with iron concentrations of less than 100 mg L^{-1}. The following laboratory experiments deal with concentrations only up to 100 mg L^{-1} for both iron and manganese.

If the forming of precipitates is unlikely, the question is how stable are water samples with low concentrations of arsenite. Preservation experiments were carried out in 10 mmol L^{-1} H_3PO_4 using 100 μg L^{-1} arsenite together with varying concentrations of iron or manganese. The experimental results for these trials are illustrated in Figs. 3 and 4. The arsenite concentration is constant for 28 days in the presence of high concentrations of both iron and manganese. Mean values and standard deviations of the three replicates for all measuring days are 100.2 ± 3.1 μg L^{-1} for iron containing sample and 102.0 ± 2.9 μg L^{-1} for manganese addition. No precipitates were observed and no arsenate was detected; which means, the aim of preserving the arsenite was successfully reached within the given range of analytical errors.

The samples taken in the field yielded different concentrations of total arsenic as well as different speciation proportions (see Table 2). One example (sample 2) is shown in Fig. 5. This sample contains about 1.4 mg L^{-1} of total arsenic, most of them in the three valence state. Fig. 5 monitors the arsenite concentrations determined in different sub-samples in dependence on the duration of storage. The aim of the experiment was to control

Table 2
Constituents of the three field samples

Sample	Fe ($mg\,L^{-1}$)	Mn ($mg\,L^{-1}$)	Ca ($mg\,L^{-1}$)	Mg ($mg\,L^{-1}$)	K ($mg\,L^{-1}$)	Cl^- ($mg\,L^{-1}$)	NO_3^- ($mg\,L^{-1}$)	SO_4^{2-} ($mg\,L^{-1}$)	pH	Eh (Mv)	T (°C)	O_2 ($mg\,L^{-1}$)
1	<0.05	0.8	61.0	7.5	10.8	4.3	2.2	154	6.5	331	8.5	11.1
2	7.7	8.1	45.0	6.2	13.0	10.6	1.1	80	6.4	243	8.4	1.7
3	5.0	6.6	48.7	6.5	12.5	9.1	1.3	95	6.5	246	8.1	8.1

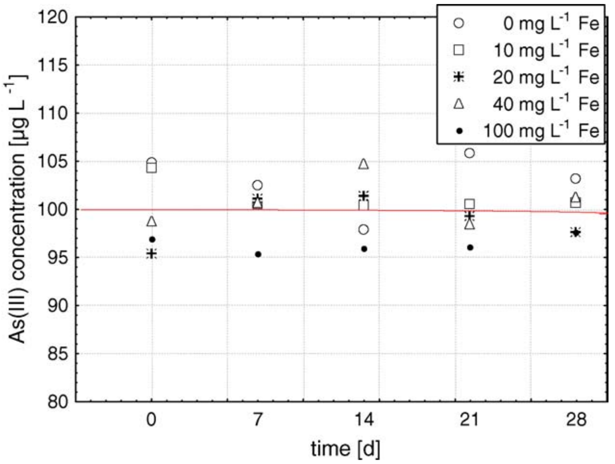

Fig. 3. Stability of a 100 $\mu g\,L^{-1}$ As(III) solution in presence of different Fe concentrations, mean values of three replicates.

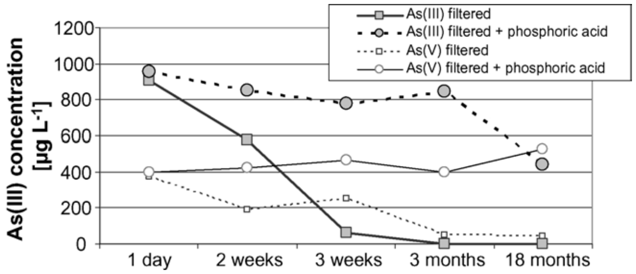

Fig. 5. Results of the preservation experiment in the field.

the stability of the species for a short storage period (up to 3 weeks) and to monitor the As concentration, when the samples are stored for either 3 or 18 months.

The complete oxidation of arsenite took place during a period of 3 weeks in the non-stabilised sample, which was merely stored cool (6 °C) and dark. The decrease of As(V) is slightly delayed due to overlapping of sorption onto iron hydroxides and the formation by oxidation of arsenite. However, after 3 months the concentration of the sum of both species is only about 5% of the initial one.

Preservation by means of phosphoric acid offers much better results in comparison to just cooling and keeping dark concerning the preservation of arsenic species. While the result after 3 months may be satisfactory, analysis after 18 months shows dramatic losses of about 50% of arsenite in the sample (see Fig. 5). The slight increase of arsenate concentration cannot explain the dramatical loss in arsenite concentration. General losses of arsenic have to be considered additionally to the shift between the two species. This illustrates that such samples cannot be preserved for very long periods of time.

The concentration of arsenic species in all samples (see Table 3) was higher than 90% of the initial value after 3 months, with the tendency towards a slight diminution of arsenite.

The total arsenic concentrations determined by ICP–AES are shown in Table 3 for comparison. The sum of the two species measured after 1 day is in good agreement with the total concentrations (difference < 6%).

The different behaviour observed between samples filtered immediately in the field and non-filtered samples is reflected in a loss of arsenic due to intensive contact of the solution with air during the filtration process. The iron hydroxides precipitated immediately on the filters, visible as a red-brown filter cake, which serves as a very effective sorbent for the removal of

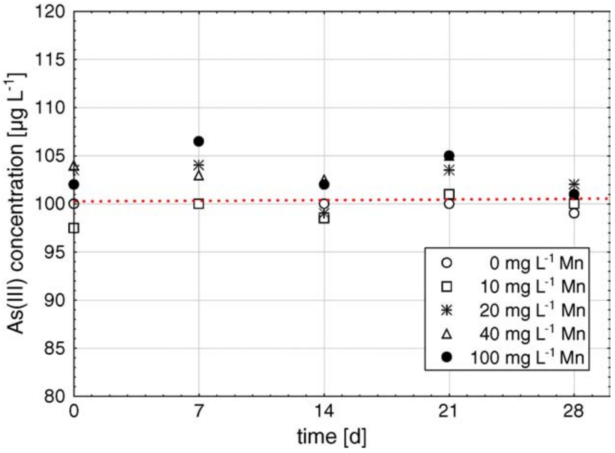

Fig. 4. Stability of a 100 $\mu g\,L^{-1}$ As(III) solution in presence of different Mn concentrations, mean values of three replicates.

Table 3
Arsenic species concentrations (in $\mu g\,L^{-1}$) in field samples 1 day and 3 months after sampling, preservation agent 10 mM H_3PO_4

Sample	Total	1 day			3 months		
	ICP–AES	As(III)	As(V)	Total	As(III)	As(V)	Total
Sample 1							
Filtered	<60	<2	39	39	<2	44	44
Non-filtered	<60	<2	31	31	<2	35	35
Sample 2							
Filtered	1270	956	400	1356	841	397	1238
Non-filtered	2980	1205	1769	2974	1153	1751	2904
Sample 3							
Filtered	934	691	266	957	624	240	864
Non-filtered	3040	732	2200	2931	656	2068	2725

arsenic. Acidification with phosphoric acid dissolves colloidal particles in the samples and avoids precipitation. Consequently, higher concentrations of arsenic will be determined. Nevertheless, the preservation of the arsenic species was successful in both types of samples.

4. Conclusions

It was shown that phosphoric acid is a suitable agent for stabilization during storage of samples containing high concentrations (up to 100 mg L^{-1}) of manganese and iron, and for the preservation of arsenic species up to 3 months. Longer storage times are not advisable. Precipitates were observed in experiments neither in the laboratory, nor in the field. The samples have to remain cool (6 °C is advisable) and dark, and the pH has to be lowered to 2 or less. In the case of water samples with a high buffer capacity, an additional amount of acid should be used to adjust the pH. As shown in a previous study [6], higher concentrations of phosphoric acid may disturb the ion chromatographic separation.

The method seems to be suitable for filtered and non-filtered samples. Colloids in the aqueous phase may adsorb arsenic resulting in a significant difference between the soluble fraction in a water sample and the total concentration including the colloidal bound arsenic. Colloids with high sorption capacities like oxyhydroxides of iron or manganese are well known as removal agents for arsenic in water treatment. Acidification with phosphoric acid can assist to avoid their formation and to long term stabilize the inorganic arsenic species in their original state.

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