

Original Paper

An Analytical Method for the Separation and Determination of As(III) and As(V) in Seepage and Acid Mine Drainage Water

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Abstract. To avoid changes in the original As species distribution in natural water after sampling, a method of immediate separation of As(V) by anion exchange at the sampling site was developed. The procedure consists of two steps. The total concentration of arsenic is determined in one part of the water sample acidified on site. Another part of the water samples is pressed through a column filled with an anion exchanger. The As(III) species that is not redox-stable remains in the effluent of the sorbents column and can be analyzed with conventional methods after stabilization by addition of conc. HNO_3 . As(V) is sorbed by the exchanger material. The As(V) concentration can be calculated as the difference between As_{sol} and As(III), neglecting very low contents of methylated species.

Oxidation of Fe(II) by air followed by co-precipitation of arsenic with iron hydroxide was applied in field experiments to minimize the As concentration in seepage and mining water.

Key words: Arsenic; speciation; oxidation; anion exchange; mining.

The geochemical behaviour and toxicity of arsenic are determined to a considerable degree by the prevailing arsenic species [1, 2]. In seepage water and acid mine drainage from ore mining, As(III) and As(V) are the

dominant species. Methylated species such as monomethylarsinic (MMA) and dimethylarsinic (DMA) acid are present in very low concentrations or not present at all. These species do not play a role in the contamination of surface waters discharged in mining areas.

Different procedures for the determination of arsenic species are described in the literature, e.g. [3, 4]. The problem is not the determination of the different species, but the preservation of the original arsenic species from the time of sampling to the point of analysis in the laboratory. As(III) is a redox-unstable species. A proportion of As(III) is oxidized within a short time (minutes to days), and according to our knowledge there is no reliable method of stabilizing the original species in the water samples [5, 6].

The causes for time-dependent variation in As species patterns in different water samples have not been sufficiently elucidated. Obviously some correlation exists between the water composition, contact with air, and the pH value. Particulate iron and manganese hydroxides could also play an important role. However, it is complicated to stabilize the original species distribution e.g. by direct filtration or preservation without any contact with air.

Figure 1 shows the Eh–pH diagram of As species predominant in several seepage and acid mine drainage water samples. Samples A, B, and C represent three typical sampling sites with different water

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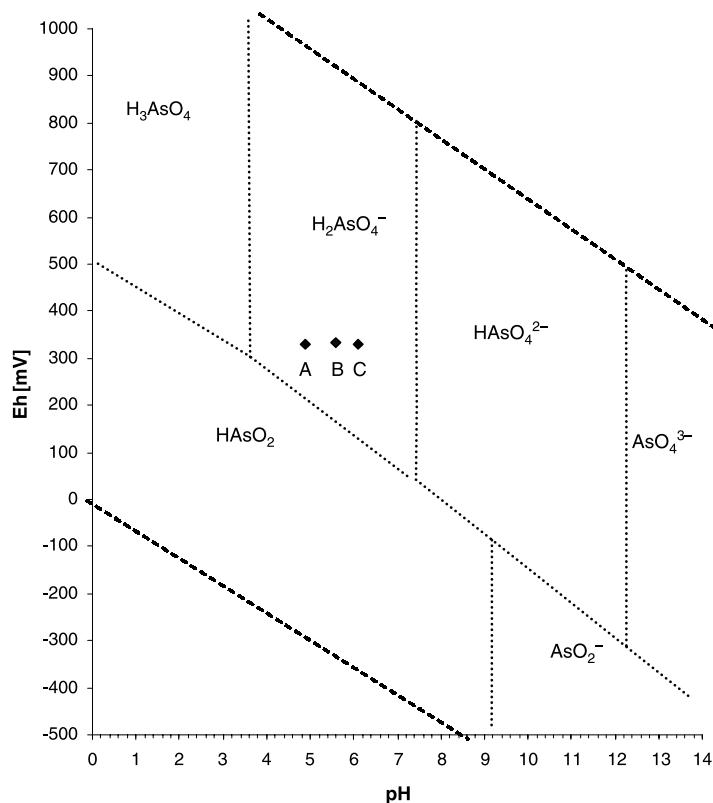


Fig. 1. Redox-pH equilibrium diagram for the system Arsenic-Water, at 25 °C and 1 atm

compositions. At Eh-pH conditions typical of seepage and acid mine drainage waters in the Ore mountains (Erzgebirge, Germany), As(V) occurs in anionic form as H_2AsO_4^- and As(III) as neutral non-dissociated acid HAsO_2 , respectively. These findings (Fig. 1) lead us to the conclusion that the separation of As(III) from As(V) employing an anion exchange technique is feasible.

In many cases acid mine drainage and seepage waters contain high concentrations of Fe(II) which is oxidized in contact with air and precipitated as iron hydroxide. This reaction was used in experiments to minimize As contamination by coprecipitation.

Experimental

Instrumental

An atomic absorptions spectrometer with a graphite furnace (4100ZL, HGA 700, Perkin Elmer) was employed for the determination of As concentrations higher than $50 \mu\text{g L}^{-1}$. For smaller As concentrations a hydride generation system (FIAS 200, Perkin Elmer) was connected to the furnace. The instrumental parameters used are presented in Table 1.

Several trace elements and main components (see Table 2) were determined by ICP-MS (ELAN 9000, Perkin Elmer Sciex) and ICP OES (Vistar, Varian), respectively.

Table 1. Parameters for arsenic determination by ETA-AAS and FIAS-Furnace-AAS

Wavelength	193.7 nm
Slit width	0.7 nm
Measurement mode	peak area
Graphite tube only	
– Matrix modifier	solution of Pd + Mg nitrate
– Ash	1100 °C
– Atomize	2000 °C gas stop
– Calibrations range	50–500 $\mu\text{g L}^{-1}$
Connection FIAS-furnace	
– Graphite tube Ir conditioned	
– Ash	400 °C
– Atomize	2100 °C gas stop
– Calibrations range	1–10 $\mu\text{g L}^{-1}$

Anion Exchange Column

A one-way syringe (20 mL) with a Luer Lock adapter and filter holder including a membrane filter was used as column. The column had been prepared in the laboratory and was filled with about 8 mL anion exchanger (amberlite IRA-402, chloride type, neutrally washed with deionized water, grain size 0.6–0.75 mm).

Reagents

All chemical reagents used were of analytical grade. HNO_3 was of suprapur (Merck) quality. Calibration solutions are prepared using the standard solutions SPEC-AS 5 for As(V) and SPEC-AS 3 for As(III) (Jobin Yvon HORIBA Group).

Table 2. Range of the chemical composition of selected seepage water samples

Sampling point Number		A 9	B 6	C 6
pH		4.2–4.9	5.6–6.2	6.0–6.7
Eh	mV	328–558	317–354	291–366
el. cond.	$\mu\text{S cm}^{-1}$	938–1370	1110–2000	658–1470
HCO_3^-	mg L^{-1}	0–6.6	34.2–68.8	3.9–12.2
SO_4^{2-}	mg L^{-1}	623–903	991–1150	341–895
Cl^-	mg L^{-1}	7.9–10.6	13.7–20.0	13.2–24.3
F^-	mg L^{-1}	9.1–22.2	7.1–12.0	5.7–11.4
Na	mg L^{-1}	10.6–11.9	18.1–21.9	11.8–18.8
K	mg L^{-1}	12.5–16.1	18.3–20.9	8.5–17.4
Ca	mg L^{-1}	137–174	243–266	91–201
Mg	mg L^{-1}	35.4–47.0	63.3–68.3	22.4–50.6
Al_{sol}	mg L^{-1}	9.9–16.2	4.5–7.4	2.3–6.5
Cd_{sol}	mg L^{-1}	<0.002–0.006	0.010–0.023	0.002–0.012
Co_{sol}	mg L^{-1}	0.33–0.37	0.12–0.18	0.07–0.26
Cu_{sol}	mg L^{-1}	0.05–0.09	0.006–0.011	0.01–0.03
Mn_{sol}	mg L^{-1}	15.4–20.2	11.9–14.5	4.4–15.7
Ni_{sol}	mg L^{-1}	0.47–0.62	0.56–0.77	0.17–0.36
Pb_{sol}	mg L^{-1}	<0.05	<0.05	<0.05
Si_{sol}	mg L^{-1}	11.5–13.4	8.6–9.5	7.2–9.3
Zn_{sol}	mg L^{-1}	8.6–13.1	5.3–17.7	3.4–7.1
As_{tot}	mg L^{-1}	1.3–5.2	1.4–1.7	0.31–1.6
As_{sol}	mg L^{-1}	0.7–4.1	1.1–1.6	0.13–0.88
$\text{As(III)}_{\text{sol}}$	mg L^{-1}	0.5–3.1	0.64–1.0	0.26–0.69
Fe_{tot}	mg L^{-1}	12.0–40.7	23.3–29.2	2.9–15.9
Fe_{sol}	mg L^{-1}	10.6–35.8	22.2–28.4	1.7–11.8
$\text{Fe(II)}_{\text{sol}}$	mg L^{-1}	10.1–35.6	19.4–28.0	1.7–11.8

Procedure for Sample Preparation

For comprehensive analysis the sample is divided into five parts.

1. Determination of total As concentration (As_{tot}) and other elements
2. Determination of solved As concentration (As_{sol}) and other elements
3. Separation and analysis of As(III)
4. Determination of Fe(II)
5. Determination of main components

To analyze the total As concentration, one sub-sample is stabilized by addition of conc. HNO_3 (1 mL/100 mL water). In the second sub-sample, the particulate matter is separated by vacuum or pressure filtration through a membrane filter (0.45 μm). This sample is further divided into four sub-samples. One of these is stabilized by addition of conc. HNO_3 and used for the analysis of solved As (As_{sol}). The second filtered sub-sample (50 mL) is used for separation and analysis of As(III), the third sub-sample is stabilized with concentrated H_2SO_4 (1 mL/100 mL water) for the analysis of Fe(II) [7].

Procedure for Separation of As(III)

To complex the iron ions 0.5 mL of 0.25 M EDTA was added to 50 mL of the fourth filtered sub sample. This sample was adjusted to pH 7–9. After removing the piston of the sorbents tube, the resulting solution is loaded onto the anion exchange column by pressing slowly the piston (flow rate 4 mL min^{-1}). The first portion of effluat (15 mL) is rejected. The main part of the effluat is stabilized with HNO_3 (65% v/v) and subsequently used for the determination of As,

which corresponds to the concentration of As(III). As(V) is retained by exchanger resin. The re-elution of As(V) is time-consuming. Therefore, this step is performed in the laboratory.

In the absence of methylated As compounds, the As(V) concentrations can be calculated as the difference between As_{sol} and As(III).

As shown in Fig. 2, the anion exchanger retains As(V) and a small part of As(III) (5–10%) with good reproducibility.

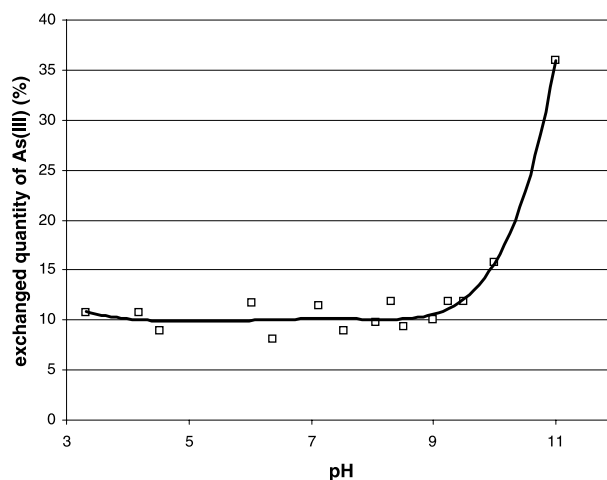


Fig. 2. Exchanged quantity of As(III) on the exchanger column dependent on the pH value

Therefore, the calibration solutions are to be treated in the same manner.

With respect to natural conditions, the influence of sulphate on the procedure was tested with a concentration of up to $1,100 \text{ mg L}^{-1} \text{ SO}_4^{2-}$. It was found that such elevated concentrations of sulphate do not affect the exchange process.

Within the pH range of 7 to 9, the method provides good results with a relative standard deviation of about 4%.

Results and Discussion

The proposed method was used for the analysis of several seepage and acid mine drainage water samples. Selected types of water samples (Table 2), characterized by high Fe(II) contents, were used to monitor the oxidation rate of As(III).

As shown in Fig. 3, there is a decrease in As(III) concentrations (without any air contact) as a function of time and pH. The reaction rate of oxidation increases with increasing pH. In sample A (pH 4.9) about 85% of the original As(III) concentration was found after 96 hours. In sample C (pH 6.1) only 26% of the original As(III) could be detected after this time interval. Under the Eh–pH conditions which exist for the selected water samples (Fig. 1), the equilibrium line between the stability fields of Fe(II) and Fe(OH)₃ is located between pH 4.8 and 5 in the corresponding diagram [8]. A similar trend is visible when increasing the pH for the oxidation of Fe(II).

The temporal changes of As_{sol}, As(III), Fe_{sol} and Fe(II) in seepage water in contact with air at pH 5.6 are shown in Fig. 4. In the initial phase, the formation and precipitation of iron hydroxide causes the preferential coprecipitation of As(V). The resulting decrease in arsenic concentration is determined by the oxidation rate of As(III). After a time interval of 144 hours the As concentration decreased from 1 mg L^{-1} to only a few $\mu\text{g L}^{-1}$. The qualitative trend of this process is equal for all sample types under investigation. However, the final state of this process is often reached after a significantly shorter time.

When applying this reaction in the field of seepage water remediation, the highest As concentration legally permitted ($100 \mu\text{g L}^{-1}$) to seep into surface water is already reached after a reaction time of 40–120 hours.

Under slightly acidic conditions and in contact with air, the oxidation of iron and the formation of iron hydroxide occurs slowly. This leads to the preferential co-precipitation of arsenic and a low concentration of As in the water. Acceleration of the oxidation rate, which can be achieved by changing the pH to basic values, results in an accelerated formation and precipitation of iron hydroxide. This leads to a reduced co-precipitation of As(V) and thus to a smaller decrease in arsenic concentration in the samples, as occurs under slightly acidic conditions. Thus, the

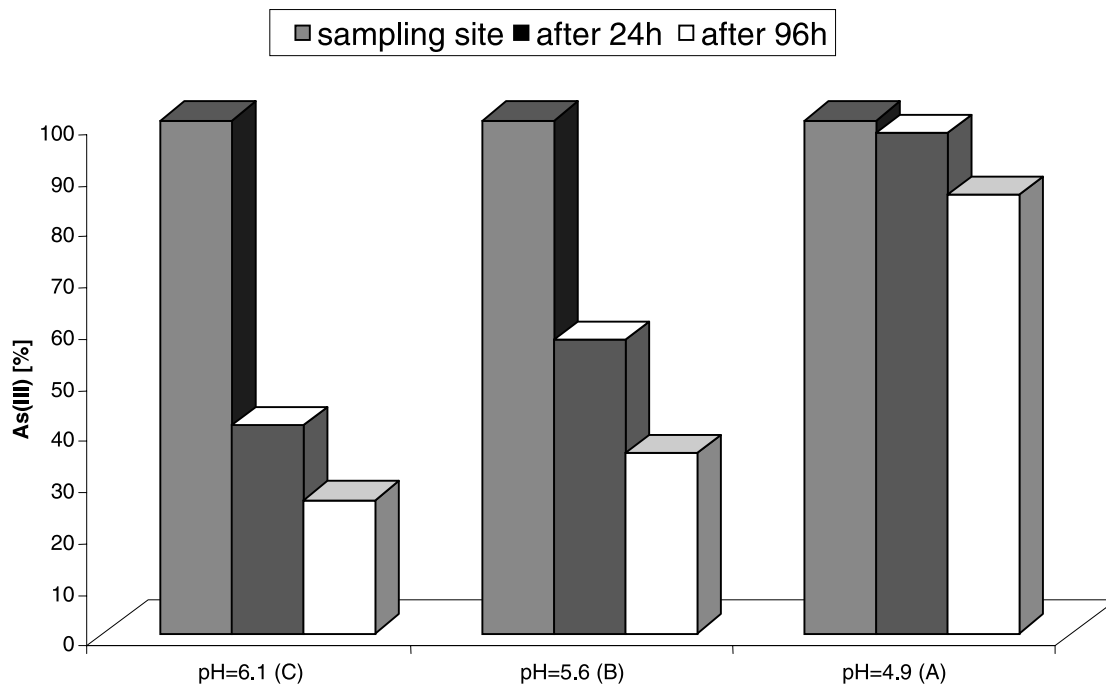


Fig. 3. Influence of pH value and test time on the decrease of As(III) content

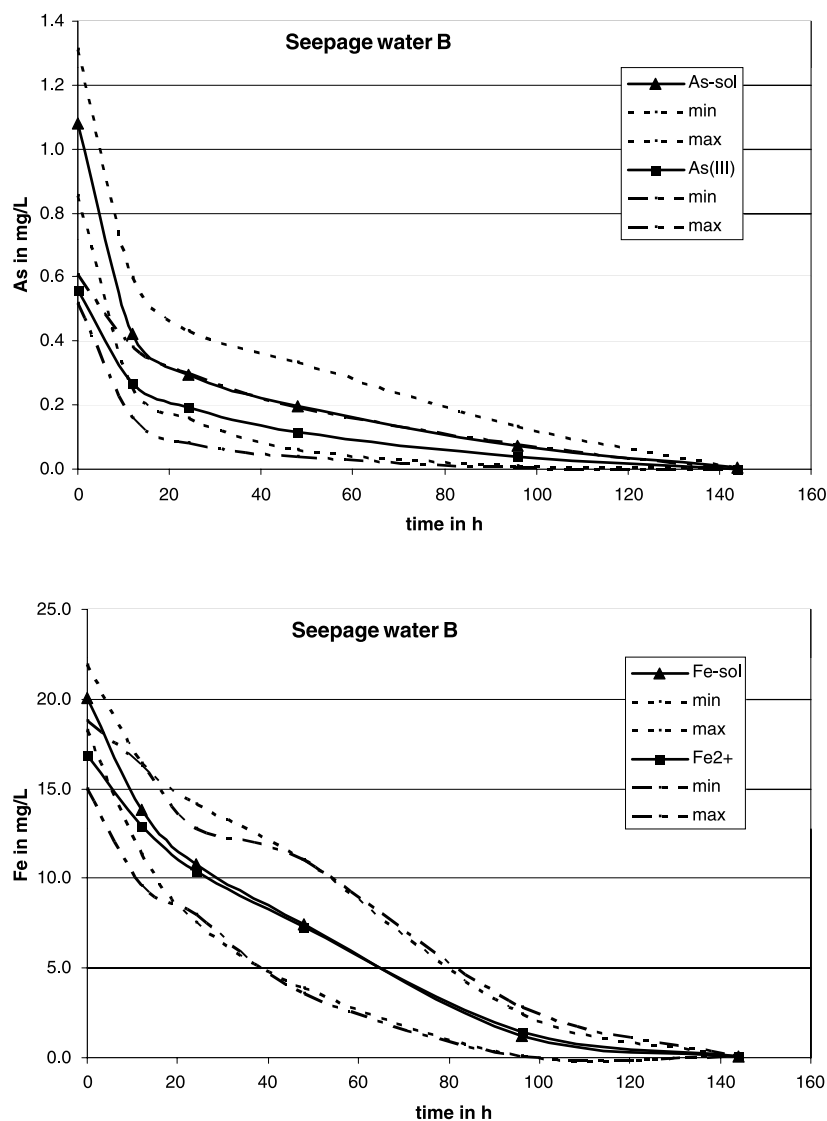


Fig. 4. Results of the experiment illustrating the precipitation behavior of As and Fe

As concentration remains in the range of 300 to 400 $\mu\text{g L}^{-1}$.

These results formed the basis of a passive purification procedure for seepage water under natural on-site conditions. In a pilot test, which has been running for 2 years now, seepage water of tin ore tailings are collected in open ditches (sample C in Table 1). After air saturation, the seepage water flows into the flooded tin mine. There the oxidation of Fe(II), the hydrolysis, and the precipitation of iron hydroxide with adsorbed arsenic take place.

Conclusion

The proposed method for the determination of As(III) based on the separation of As(V) from samples by anion

exchange immediately at the sampling site could be successfully used for seepage and acid mine drainage. It can be accomplished with simple equipment. As(III), which remains in the sample, can be analyzed with normal analytical methods such as AAS, ICP-AES, and ICP-MS. If methylated As species are not present in the water sample, the concentration of As(V) can be calculated as the difference between As_{sol} and As(III). The coprecipitation of arsenic with iron hydroxide takes place preferentially with As(V). Natural water samples are characterized by different reaction rates of As(III) and Fe(II) oxidation. However, in general the concentrations of arsenic reach a level which is lower than 100 $\mu\text{g L}^{-1}$ after 40–120 hours. (This is the highest value permitted by the German legislation for the input of contaminated water from mining areas into surface water.)

This reaction can be used as a passive method of water purification as is shown in pilot tests under real mining conditions.

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