Talanta 105 (2013) 46–51

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Preparative separation of arsenate from phosphate by IRA-400 (OH) for oxygen isotopic work

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ARTICLE INFO

Article history:
Received 6 September 2012
Received in revised form
19 November 2012
Accepted 24 November 2012
Available online 30 November 2012

Keywords:
Preparative separation
Arsenate
Phosphate
IRA-400 (OH)

ABSTRACT

The paper reports about a series of tests carried out to find out the optimal conditions for the preparative separation of arsenate and phosphate from natural waters, using the anion exchange resin Amberlite IRA-400 (OH). Freundlich isotherms have been constructed on basis of data obtained by stirring different amounts of resin (0.05–1.00 g) with solutions containing 1 mg/L As and 10 mg/L P in form of arsenate and phosphate and the effect of pH and P/As ratio on adsorption was investigated. It was found that at these concentrations 0.5 g of IRA-400 (OH) can adsorb quantitatively arsenate and phosphate within 1 h. In a range of 3.6–11.1, pH seems to have no influence on the adsorption behavior of the resin, but at pH 1.5 the adsorption of both arsenate and phosphate drops to values close to zero. Experiments with solutions with P/As ratios in a range between 1 and 30 have shown that the concentration ratios have also little effect on adsorption. An efficient selective desorption of the anions could be achieved with 2 mol/L HNO_3 or HCl, but the use of HCl is impracticable if the separation aims at precipitating arsenate for oxygen isotopic work. The reported adsorption/ desorption properties of the resin are supported also by data obtained by investigating the resin particles with a scanning electron microscope equipped with a fluorescence detection device.

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1. Introduction

Natural contamination of groundwater by arsenic became a crucial water quality problem in many parts of the world. The scale of the problem is notably grave in parts of South and East Asia e.g. [1–6]. Despite the progress in elucidating the cause of this calamity, many questions are still open. Redox seems to be a major actuator in releasing arsenic from sediments into the groundwater, but the association of As hot-spots with low redox environments is not always unequivocal. It was suggested that in some cases the release of arsenic from the sediments occurs at a site different to that in which the elevated concentrations in groundwater are observed [7].

A new approach to constrain the source and site of arsenic release was proposed by Berner et al. [8], by investigating and comparing the isotope composition of oxygen in arsenate and arsenite dissolved in groundwater with that adsorbed to the aquifer sediments. In addition to the pre-concentration of the oxianionic As-species, prior to their separation and precipitation as Ag-arsenate and Ag-arsenite, respectively (which are subsequently used for the isotopic work), the approach requires also their quantitative separation from other oxygen bearing anions, like phosphate, sulfate, (bi)carbonate, which otherwise would interfere with the measurement of the isotopic composition of the arsenic-bound oxygen.

A routinely applied method for separation of arsenite and arsenate in the field is that of Meng et al. [9], which is based on the selective and rapid retention of As (V) oxyanion on an alumino-silicate based sorbent. The efficiency of these cartridges in terms of the recovery of the As (III) in the filtrate, as determined by the authors, was found to be 95–98%. On the other hand, it could be also shown [8] that this technique allows also an efficient separation of other oxyanionic species, with phosphate being co-adsorbed with arsenate, whereas nitrate and sulfate (as well as chloride) pass together with arsenite practically unhindered the cartridge. Although the authors do not give any details on the composition of the sorbent, the separation is based obviously on the property of arsenate and phosphate to form strong inner-sphere complexes on aluminosilicates [10]. According to the pH dependent equilibrium conditions in the aquatic carbonate system [11], (bi-) carbonate can be easily removed as CO_2 by lowering the pH below 4.3. However, considering the close similarity in the chemical behavior of arsenate and phosphate, the quantitative separation of these two anions is a more challenging task, the more if the initial isotopic composition of the associated oxygen atoms must be not

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http://dx.doi.org/10.1016/j.talanta.2012.11.069

changed during the procedure. Several methods [12–14] were developed to separate arsenate and arsenite for online measurement without influences of those foreign ions, but no report compared the oxyanions concentration during the experiment processes. Ross et al. [15] used a butanol–chloroform mixture to separate phosphate from arsenate and got up 96% phosphate extracted, but the extract contained also 13% of the arsenate present initial in solution.

The Amberlite IRA-400 is a macroporous strong basic anion exchange resin with a large application field and it was used to remove anions like nitrate, chromate and phosphate from solutions [16–23]. It was also shown that the adsorption behavior of phosphate on different forms of amberlite IRA-400 (Cl^-, Br^-, NO_3^-, SO_4^{2-}) is almost similar, but the ratio of the exchanged anions (chloride, bromide, nitrate or sulfate) to the amount of adsorbed phosphate increases with the increase in pH and decreases with the concentration of phosphate in solution. The reason for this behavior must be sought in the electroselectivity of the resin. In a pH range between 3 and 11, the ionic species of phosphate in solution are $H_2PO_4^-$ ($pK_1=2.15$), HPO_4^{2-} ($pK_2=7.20$) and PO_4^{3-} ($pK_3=12.38$). From a dilute solution, the resin prefers to adsorb the ion with the highest charge (PO_4^{3-}), consequently the sorption of phosphate increases with increasing pH. However, no papers have been found that report about to use of IRA-400 for the selective separation of arsenate from phosphate.

The aim of this study was to verify the suitability of IRA-400 (OH) for such a purpose and to develop a procedure to obtain arsenate adequate for isotopic work. Because even in high arsenic groundwater total As concentrations do not exceed 1–2 mg/L and the As(III)/As(V) ratios are usually high, in addition to separation from other oxyanionic species, it appears mandatory that a proposed procedure allows a pre-concentration of arsenate prior to its precipitation as Ag-arsenate. The basic idea is to load an adequate amount of arsenate onto the cartridge proposed by Meng et al. [9] by passing a sufficiently large volume of groundwater through the cartridge and after leaching the anions from the column, separate arsenate and phosphate by means of amberlite IRA-400 (OH). We report here about this step in which we try to fathom out the optimal conditions by which the two anions can be separated by selective stripping after being previously loaded onto the amberlite.

2. Materials and methods

The Amberlite IRA-400 (OH) (16–50 mesh) (Sigma–Aldrich) is a strong base, anion exchange resin with a quaternary ammonium functional group, with the main characteristics given in Table 1. In order to remove trace impurities, before use, the resin was firstly washed with de-ionized water (18.2 MΩ cm MilliQ), and then with 0.25 mol/L NaOH until no chloride could be detected in the effluent. Stock solutions of 100 mg/L As (V) and 1 g/L P (V) were prepared by dissolving $Na_2HAsO_4 \cdot 7H_2O$ (p.a. Merck), and KH_2PO_4 (p.a. Merck), respectively. 65 vol% HNO_3 (Suprapure, VWM) and NH_4OH (Merck) were used to adjust the pH to the required values in the different steps of the experiments. For the desorption experiments eluents with different concentrations were prepared from 32 vol% NaOH (p.a. Roth), 37 vol% HCl (p.a.Roth) and 96 vol% CH_3COOH (p.a. Merck).

Table 1
Characteristics of IRA-400 (OH).

Limit	**60 °C max. temperature**
Cross-linkage	8%
Moisture	~45%
Matrix	Styrene–divinylbenzene (gel)
Particle size	16–50 mesh
Operating pH	0–14
Capacity	1.2 meq/mL by wetted bed volume

Arsenate was quantified by measuring the As concentration by fluid injection atomic spectrometry (FIAS 400; Perkin–Elmer), whereas phosphate concentrations were determined colorimetrically by the ammonium-molybdate method, according to DIN EN ISO 6878-D11. Except for chloride, other relevant anions were measured by ion-chromatography (ICS 1000; Dionex). The chloride concentrations at very low or very high pH were assessed photometrically (Merck), using a field kit (Merck) with a detection range between 5 and 125 mg/L Cl^-. The elemental composition of the resin particles was determined by energy dispersive X-ray fluorescence analysis (ED-XRF, Spectra 5000, Atomica). Scanning electron microscopy coupled with an X-ray fluorescence detection device (SEM-XRD) (Zeiss DSM 960) was used to characterize qualitatively the surface of the loaded and subsequently leached resin particles.

The kinetic experiments were carried out by shaking 1 g of IRA-400 (OH) resin for different time intervals (up to 2 h) with 250 mL of solution containing 1 mg/L As and 10 mg/L P. Such an As/P ratio is typical for many sites with high As groundwater [24,25]. To improve the interaction between solutes and sorbent, a magnetic stirrer, operated at 300 rpm, was applied. Sorption capacity was determined by treating solutions (250 mL) of different concentrations (10 mg/L P; 1 mg/L As; 10 mg/L P+1 mg/L As) with variable amounts of resin (0.05 g, 0.10 g, 0.20 g, 0.30 g, 0.40 g, 0.50 g, 0.60 g, 0.70 g, 0.80 g, 0.90 g and 1.00 g) under conditions similar to those in the kinetic experiments. The effect of pH on the adsorption was investigated using solution batches (250 ml), buffered in a pH range between 1.5 and 11 and stirred with 1 g of resin for 1 h at 300 rpm. All the experiments were done at 21 ± 1 °C. The actual conditions are specified in results part and in the caption of the figures.

3. Results and discussion

3.1. The sorption capacity of IRA-400 (OH) for arsenate and phosphate

The time necessary for a quantitative adsorption of arsenate and phosphate by 1 g of resin from a solution containing 1 mg/L

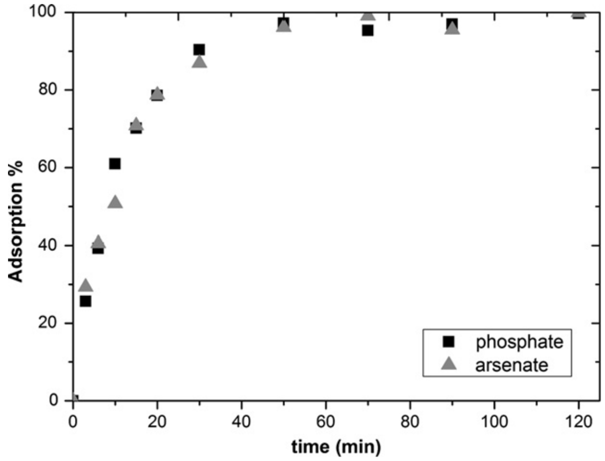

Fig. 1. Adsorption kinetics of arsenate and phosphate by IRA-400 (OH). Experimental conditions: 1 g IRA-400 (OH) resin, 250 ml of solution with 10 mg/L P and 1 mg/L As, pH 5.5.

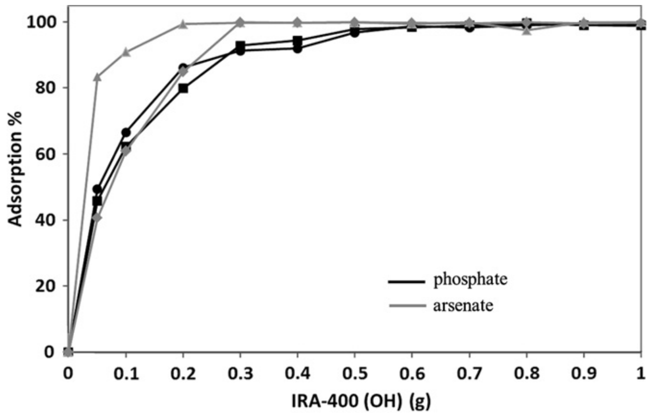

Fig. 2. Adsorption of arsenate and phosphate by different amounts of IRA- 400 (OH). Experimental conditions: ●: the adsorption of phosphate in solution with 10 mg/L P; ■: the adsorption of phosphate in solution with 10 mg/L P+1 mg/L As; ▲: the adsorption of arsenate in solution with 1 mg/L As; ◆: the adsorption of arsenate in solution with 10 mg/L P+1 mg/L As. pH 5.5, stirring time 2 h at 300 rpm.

As and 10 mg/L P is shown to be slightly less than 1 h (Fig. 1). Up to about 20 min, the adsorption increases almost linear with time, to diminish afterwards and levels off close to 100% after 1 h.

Results of the experiments to find out the optimal amount of resin necessary for a complete elimination of arsenate and phosphate are shown in Fig. 2. After addition of the resin, the initial pH of the solution aliquots was around 5.5. It was found that—a minimum of 0.5 g of resin is necessary for a quantitative removal of both phosphate and arsenate from solutions with the specified compositions). However, considering that the actual aim of the study is to find out the optimal conditions for the quantitative extraction of arsenate, only, apparently, already 0.3 g of resin is sufficient for this purpose. It also can be seen that, compared to phosphate, the removal of arsenate is slightly more efficient, which is even more evident if the solution contains only arsenic. However, this may be due to its lower concentration and the competition in sorption between As and P, and not to a basically different adsorption behavior of the two anions.

The experimental data have been used also for generation of adsorption isotherms. The amount of the adsorbed anions q (mg/g) at equilibrium is given by:

$$q=(C_0-C)v/m \tag{1}$$

where C_0 (mg/L) is the initial ion concentration, C (mg/L) is the concentration at equilibrium, v (L) is the volume of the solution and m the mass of the resin (g) added. The observed adsorption trends for both arsenate and phosphate fit well a Freundlich isotherm [26], which applies to both multilayer sorption and non-ideal sorption on heterogeneous surfaces. The Freundlich isotherm is expressed by the equation:

$$q=kC^{1/n} \tag{2}$$

which may be written in a linearized form as:

$$\log q=\log k+1/n\log C \tag{3}$$

where n and k are the Freundlich constants.

The Freundlich isotherms constructed with the obtained results are shown in Fig. 3, while the linear correlation coefficients between the experimental data and the modeled isotherms are given in Table 2. The slopes of the plots of log q versus log c, for both arsenate and phosphate, were found to be very similar (Fig. 3).

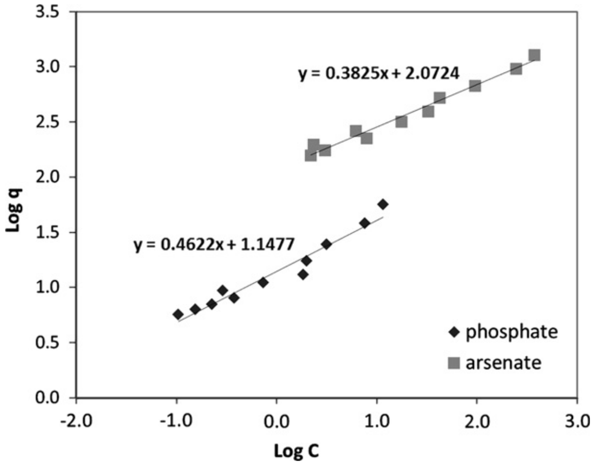

Fig. 3. Linearized Freundlich isotherms (Eq. (3) for arsenate and phosphate adsorbed by Amberlite IRA-400 (OH). Experimental conditions: 250 mL of solution with 1mg/L As and 10 mg/L P, pH 5.5, and different amounts of adsorbent (0.05–1 g).

Table 2
Parameters of Freundlich isotherms for the adsorption of arsenate and phosphate by Amberlite IRA-400 (OH).

Parameters	Arsenate	Phosphate
k	118.1	14.05
n	2.614	2.164
r^2	0.977	0.951

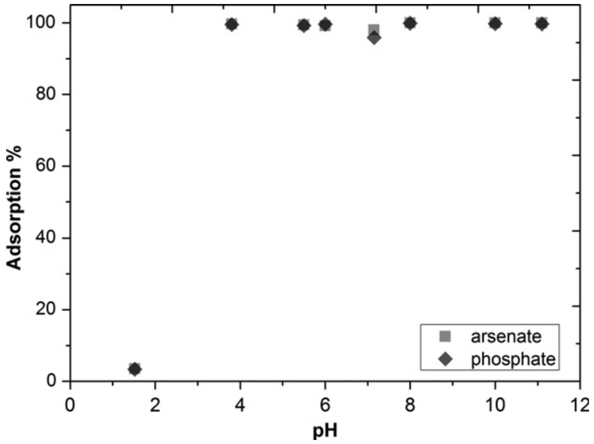

Fig. 4. Sorption of arsenate and phosphate by IRA-400 (OH) as a function of pH. Experimental conditions: 250 mL of solution with 1mg/L As and 10 mg/L P, 1 g IRA-400 (OH) resin, stirring time 1 h at 300 rpm.

3.2. The effect of pH and P/As ratio on sorption

Solution batches with identical initial arsenic and phosphorus concentrations (1 mg/L and 10mg/L, respectively) but different pH (the pH value from 1 to 11) was used in experiments to investigate the effect of protonation on the concomitant sorption of arsenate and phosphate by IRA-400 (OH) (Fig. 4). At values between 3.8 and 11.1, after 50 min, almost all arsenate and phosphate (up to 98%) was adsorbed, with no noteworthy differences in the trend of the sorption curves at different pH. At pH 1.5, however, no adsorption was observed neither for arsenate nor for phosphate. This similarity is most likely due to the wide analogy in protonation state and the correspondent electric charge of the aqueous As (V) and P (V) species at different pH values. At a pH around 1, both As and P are uncharged as

$H_3AsO_4^\circ$ and $H_3PO_4^\circ$, respectively, to pass almost simultaneously to bi-, mono- and de-protonated oxyanions, with a correspondent change in charge as pH increases. Consequently, due to their very similar adsorption behavior, P (V) - and As (V)-oxyanions cannot be separated by a pH dependent selective sorption on IRA-400 (OH).

The effect of the P/As ratio on sorption was investigated by keeping the As concentrations constant at 0.2 mg/L (close to values encountered frequently in As contaminated groundwaters), and increasing the P concentration from 0.2 mg/L to 6.0 mg/L. In a P to As ratio range of 1–30 no significant differences in the adsorption of the two anions was observed (Table 3). The sorption is close to 100% for both, but while the adsorption of arsenate is constantly around 97.7 ± 0.7%, the sorption efficiency for phosphate decreases slightly from 100% to 97.1%, as P concentration increases from 0.2 mg/L to 6.0 mg/L On the other hand, as shown before, from a solution containing 1 mg/L of As and 10 mg/L P (Fig. 1), 96.8% and 98.7% of phosphate was adsorbed after 50 and 70 min, respectively, while using a solution with 0.2 mg/L As and 6.0 mg/L P (not shown in the manuscript) 97.1% of the P was adsorbed after 60 min. Consequently, it appears that in the range of the sorption capacity of 1 g IRA-400 (OH), neither the As/P ratio nor the initial P concentration have a noteworthy effect on the removal of arsenate and phosphate from a solution.

3.3. Selective desorption of arsenate and phosphate from IRA-400 (OH)

The actual separation of arsenate and phosphate was achieved by their selective desorption from the resin. In these experiments, different eluents (NaOH, NH_4NO_3, CH_3COOH, HCl, and HNO_3) and concentrations (0.5, 1.0, 2.0 mol/L) were applied to find out the optimal conditions for separation of the anions (Fig. 5 and Fig. 6). Under alkaline conditions (250 ml of 1 mol/L NaOH), arsenate was stripped to 87%, whereas phosphate was removed quantitatively from the resin. In contrast, by leaching the resin with a 1 mol/L NH_4NO_3 solution, the situation was the other way around: arsenate was removed completely, while phosphate was recovered only to 88%. Using a weak acidic solution (0.5 mol/L CH_3COOH) only 30% of the arsenate and 45% of the adsorbed phosphate could be recovered, but the desorption increased to 60–65% for both anions when the concentration of acetic acid was raised to 1 mol/L (Fig. 6). 92–97% of both anions were also released from resin in 0.5 mol/L strong acid (HCl or HNO_3). These results show that arsenate and phosphate can be not desorbed selectively neither under alkali conditions nor using diluted acid solutions. An effective separation could be achieved, however, by further increasing the acidity of the leaching solutions to 1 mol/L HNO_3 and HCl, respectively, by which 99% of the arsenate, but only maximum 5% of the phosphate was desorbed from the resin (Fig. 5). The efficiency of the separation could be further improved when the concentration of HCl or HNO_3 was increased to 2 mol/L (Fig. 6). Under these conditions phosphate was below detection limit (< 0.01 mg/L) in the leachate, whereas arsenate was released to 99%. Subsequently, after adjusting the pH to 7.5 and adding in excess $AgNO_3$ 94.5% of the arsenate could be precipitated as Ag-arsenate from this solution. Because, as shown above (Fig. 4), at pH < 2 there is no ion exchange neither with arsenate nor with phosphate, the question arises what is the reason for their still distinct behavior when the loaded resin is treated with strongly acidic solutions. Firstly, it should be taken into account, that the bond of As and P with H^+ is much stronger than their bonding with the matrix of the IRA-400 (OH) resin ($R_zNR_3^+$). This could explain why the desorption of both As and P was almost complete using diluted strong acids with pH < 1 (0.5 mol/L HCl or HNO_3), but is not able to give account of why all arsenate but no (or at best only up to 5%) phosphate was released from the resin at even higher proton concentrations. Although, the mechanism of the desorption under such conditions is still unclear, these results suggest that the desorption of arsenate and phosphate from the resin can be not due solely to a change in charge, i.e. to ion exchange processes (see below).

Table 3
Adsorption behavior of IRA-400 (OH) under different ratios of As/P.

Ratio of As/P	As (mg/L)/P (mg/L)	P (V) adsorption (%)	As (V) adsorption (%)
1:1	0.2/ 0.2	100.0	96.6
1:2	0.2/ 0.4	99.6	98.3
1:10	0.2/ 2.0	97.5	98.2
1:30	0.2/ 6.0	97.1	97.8

Experimental conditions: 250 mL of solution with different concentration of arsenate and phosphate, 1 g IRA-400 (OH) resin, stirring time 1 h at 300 rpm.

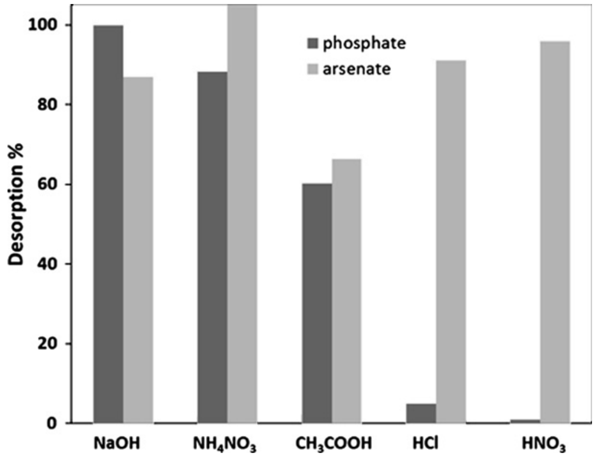

Fig. 5. Efficiency of selective arsenate and phosphate desorption from IRA-400 (OH) with different eluents in 1 mol/L concentrations.

3.4. Scanning electron microscopy combined with X-ray spectroscopy (SEM–EDX)

SEM–EDX was used to record and document changes in elemental composition on the surface of the resin grains during the different steps of the separation procedure (Fig. 7). In line with the organic matrix of the ion exchanger (styrene–divinilbenzene gel), the unloaded grains are characterized by high peaks for carbon and oxygen (Fig. 7a). The presence of chlorine is due most likely to leftovers from the manufacturing process, during which, the chloride form of the resin was transformed into the (OH) form. Further on, by means of EDXRFA small amounts of Ca, K, S and Al could be detected in the resin (Table 4). After one hour of shaking with a solution with 1 mg/L of As (V) and 10 mg/L P (V), the EDX spectrum shows clearly the loading of these elements on the surface of the grains (Fig. 7b). The leaching with 250 mL of 2 mol/L HNO_3, causes the disappearance of the As and also of Cl peaks (Fig. 7c), but not that of P. The retention of P in form of a distinct mineral phase is indicated by the occurrence of particles with high P content adhered to the surface of the beads (Fig. 8). This compound, which was not found neither in the original resin nor after the adsorption of As and P, could be a possible explanation for why P could be not eluted from IRA-400 (OH) resin by 2 mol/L HNO_3 solution. Unfortunately, these particles were too small to be characterized more accurately with methods to our disposal.

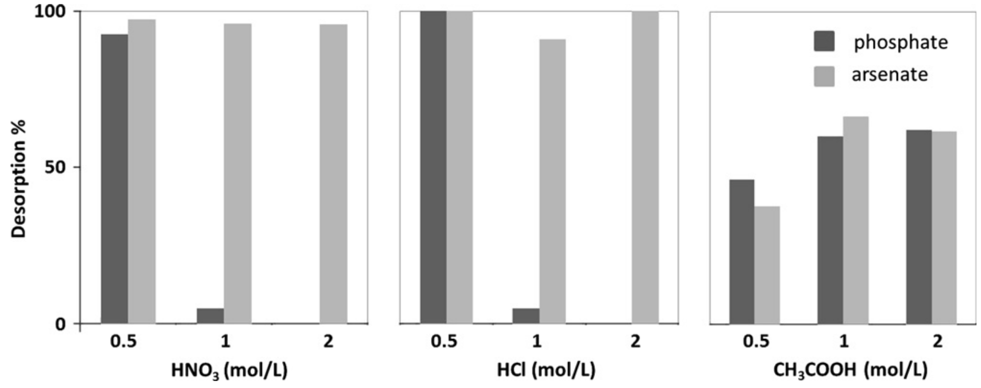

Fig. 6. Efficiency of arsenate and phosphate separation using different concentrations of HNO_3, HCl and CH_3COOH as eluents.

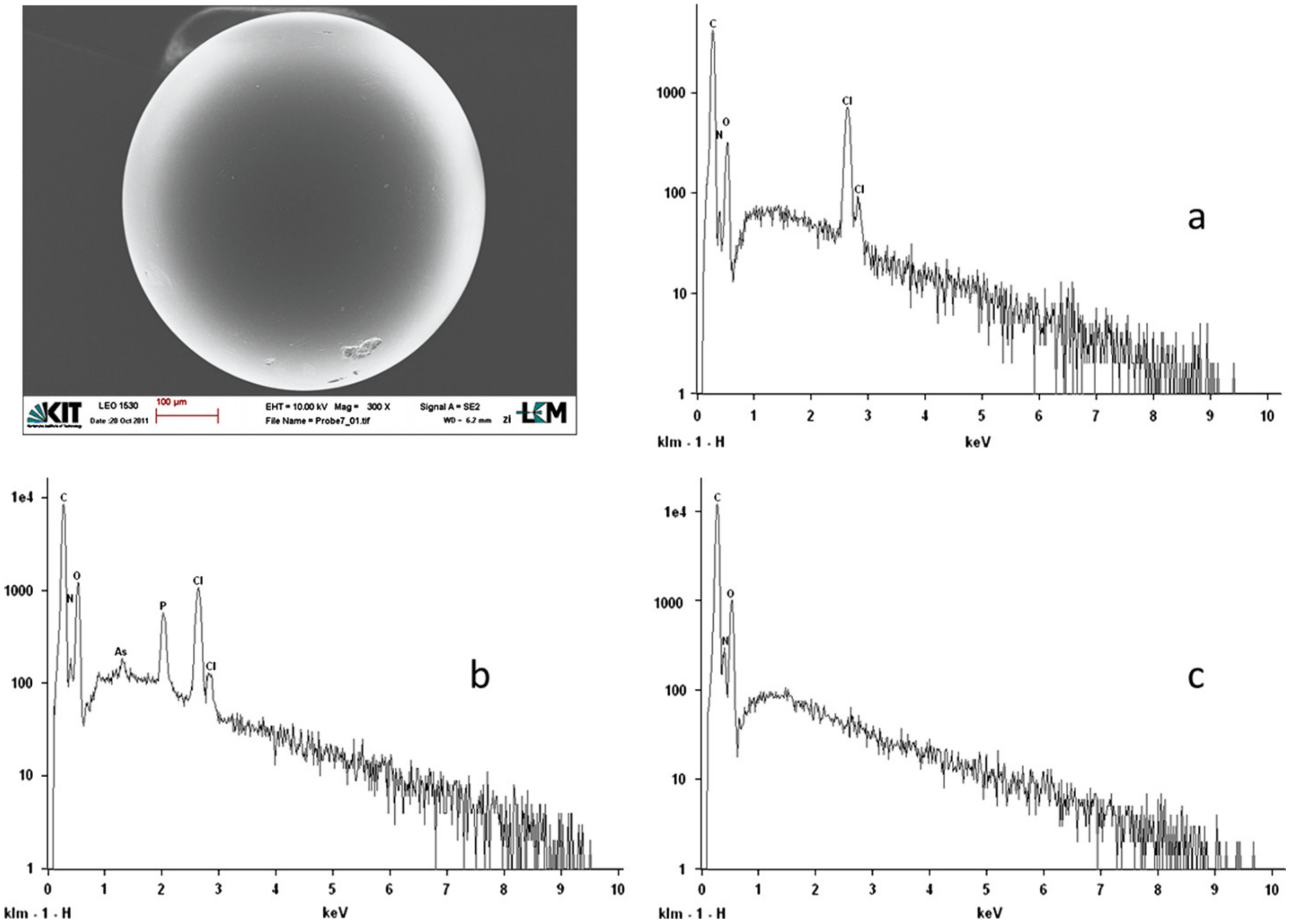

Fig. 7. SEM micrograph of an IRA-400 bead and EDX-spectra produced by the grain surface in different steps of the separation experiment: (a) before adsorption; (b): after loaded with both phosphate and arsenate; (c) after desorption with 2 M HNO_3. Analytic scale: 100 µm.

Table 4
ED-XRF data of IRA-400 beads before adsorption.

Compound	Concentration
Cl (ppm)	**141000**
Al_2O_3 (%)	1.3
K_2O (%)	0.022
CaO (%)	**0.016**
Cu (ppm)	10
Zn (ppm)	14
Ti (ppm)	12

4. Conclusion

Tests carried out with the Amberlite IRA-400 (OH) have shown that this resin can be used successfully for the preparative separation of arsenate and phosphate, a mandatory step in determination of the isotopic composition of arsenate-oxygen. After getting rid of disturbing anions like arsenite, sulfate and chloride, by applying, for example, a procedure like that proposed by Meng et al. [9], arsenate and phosphate extracted from large volumes of water can be loaded subsequently onto 0.3–0.5 g of

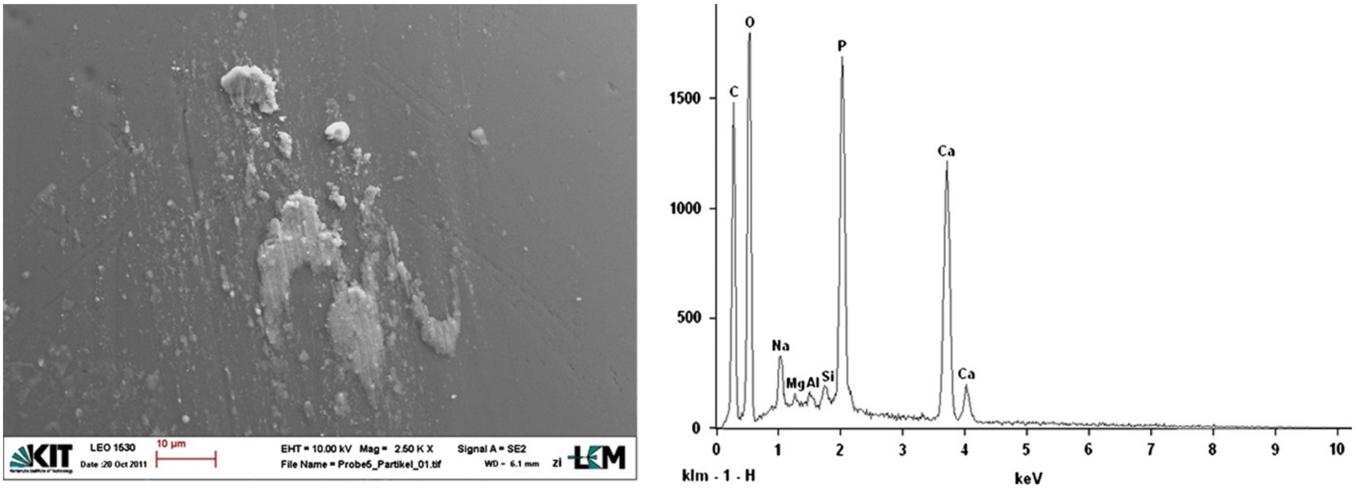

Fig. 8. SEM micrograph of the IRA-400 bead surface and EDX spectrum of a particle adhering to the surface of the resin after eluted with 2 M HNO_3. Analytic scale: 10 µm.

amberlite. Such a procedure would imply the leaching of the arsenate and phosphate caught by the alumino-silicate adsorbent of the Menǵs cartridge with a small volume of 1 mol/L NaOH solution (data not shown). This would allow not only the removal of disturbing anions (other oxianions, chloride), but also a pre-concentration of the very low arsenate contents, as found in groundwaters, even if polluted with As after adjusting the pH to >3.6, arsenate can be loaded (together with phosphate) on IRA-400 beads, from which it can be selectively stripped with 2 mol/L HNO_3. While phosphate concentrations in the leachate were found to be below detection limit, arsenate passed quantitatively into solution, from which, subsequently, 94.5% of arsenate was precipitated as Ag-Arsenate. In order to avoid the release and co-precipitation of disturbing anions, like chloride, the resin must be thoroughly clean-washed by diluted concentration (like 0.25 mol/L) of NaOH before use.

Acknowledgments

This study was supported by the German research Foundation (DFG) funding “The isotopic composition of oxygen in arsenate/arsenite: a new approach to constrain the source of arsenic in groundwater”. We would like to thank Utz Kramar and Volker Zibat for assistance in measurement at ED-XRF and EDX-SEM. Xiaohui Tang was partly financially supported by the China Scholarship Council.

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