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Overcoming matrix interferences in ion-exchange solid phase extraction of As, Cr, Mo, Sb, Se and V species from leachates of cement-based materials using multiple extractions

Mesay Mulugeta[a], Grethe Wibetoe[a,*], Christian J. Engelsen[b], Walter Lund[a]

[a] Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway
[b] SINTEF Building and Infrastructure, P.O. Box 124 Blindern, N-0314 Oslo, Norway

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ABSTRACT

Solid phase extraction (SPE) methods based on multiple extractions have been developed to overcome matrix interferences in the charge-based fractionation analysis of As, Cr, Mo, Sb, Se and V leached from cement-based materials. Disposable SPE tubes packed with 500 mg strong anion-exchange (SAX) or strong cation-exchange (SCX) sorbents were used to extract the anionic and cationic species of the elements, respectively. The multiple extractions were based on the percolation of a small sample volume (5.0 mL) through a series of identical ion-exchange tubes. For most of the elements, more than 90% of the anionic species were extracted from a sample containing up to 16 g L^{-1} NO_3^- by passing the aliquot through five identical SAX tubes. Percolating a sample aliquot through three identical SCX cartridges gave more than 99% retention for Cr(III) from leachates containing a high concentration of interfering metal cations. The anionic and cationic analytes showed only slight non-specific adsorption on the SCX and SAX sorbents, respectively, except for V(V) on the SCX sorbent. A condition was established for the quantitative elution of the retained analytes from the ion-exchange sorbents with 1.0 mol L^{-1} HNO_3. The multiple ion-exchange SPE procedures were validated using spike recovery tests. The methods were used to determine the anionic and cationic fractions of the target elements in concrete leachates covering a broad range of pH (3.8–13.4). The elements were found to exist predominantly as anions in the alkaline and neutral leachates. A high fraction (85%) of cationic Cr was detected in the most acidic leachate (pH 3.8).

1. Introduction

Evaluating the possible release of toxic elements is useful to ensure the environmentally acceptable application of recycled waste materials. In most studies, such evaluations are conducted based on the determination of the total element concentration leached from the materials. However, the release and transport mechanisms and the potential impact of the elements depend on their speciation. Therefore, determining the element species according to their specific chemical forms or physico-chemical properties will give more relevant information. In our previous study [1], an anion-exchange solid phase extraction (SPE) method was developed for the determination of the anionic species of As, Cr, Mo, Sb, Se and V leached from cement-based materials. The mentioned elements form oxyanions [2] which, under certain conditions, feature enhanced release from cement-based materials [3–5].

The cement mortar and concrete leachates analysed in the mentioned study [1] were prepared according to a standard pH-dependent leaching test [6]. The leachates at the “natural pH” of the materials were prepared using deionised water as a leachant, and leachants acidified with HNO_3 were used to generate the leachates of pH 3–12. It was found that most of the elements predominantly exist as anions in the “natural pH” leachates. Very low concentrations of anions were found in the leachates prepared using the acidified leachants. Further studies, however, revealed that the SPE of the anionic species from the latter leachates was affected by the interference from NO_3^-, which led to an underestimation of the anionic fractions [7].

In the present study, procedural modifications were devised for the previously developed anion-exchange SPE method [1] to overcome the interference from NO_3^-. The procedure was based on multiple extractions using a series of identical anion-exchange SPE sorbents. In addition, a cation-exchange SPE method was optimized for the fractionation analysis of positively charged species. Both methods were validated using spike recovery tests, and were then used to analyze leachates generated from a concrete material. The target elements in the sample solutions, SPE effluents and eluates

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[*] Corresponding author. Tel.: +47 22855516; fax: +47 22855441.
E-mail address: grethe.wibetoe@kjemi.uio.no (G. Wibetoe).

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were determined by inductively coupled plasma mass spectrometry (ICP-MS).

2. Experimental

2.1. Instrumentation

An ELAN 5000 ICP-MS instrument (Perkin-Elmer, Norwalk, USA) was used. The mass-to-charge ratios monitored were 75 (As), 53 (Cr), 98 (Mo), 121 (Sb), 77 (Se) and 51 (V). The optimum analytical conditions were the same as those used in our earlier studies [1,8]. A Varian Vista AX CCD simultaneous axial view ICP-AES (Varian Ltd, Australia) was used for the determination of the metal cations in the leachates and SPE effluents (Section 3.3). The concentration of NO_3^- in the samples was measured using a Hach DR/2010 spectrophotometer (Hach Company, Loveland, USA); the procedure is described elsewhere [9].

2.2. Ion-exchange sorbents and sample application

A polymer-based strong anion-exchanger (Extract-Clean SAX, Alltech) and a silica-based strong cation-exchanger (Bond Elut JR SCX, Varian) were used for the extraction of the anionic and cationic analyte species, respectively. The SAX sorbent was packed in a syringe barrel and the SCX in a cartridge; each had 500 mg resin. The active sites of the SAX and the SCX were quaternary ammonium and sulfonate groups with CH_3COO^- and H^+ counter-ions, respectively. The SAX had an ion-exchange capacity of 1.5 mequiv. g^{-1}, a resin of 75–150 μm particle size and a reservoir volume of 10.0 mL. The ion-exchange capacity of the SCX was 0.6–0.9 mequiv. g^{-1}, and it had a resin of 47–60 μm particle size with average pore diameter of 60 Å.

Solutions were manually loaded onto the SAX barrel, and a peristaltic pump (Minipuls 3, Gilson, Paris) connected to the outlet of the barrel was used to percolate the solutions through the sorbent. Solutions were delivered and percolated through the SCX using a peristaltic pump connected to the cartridge.

2.3. Chemicals, reagents and working solutions

Stock standard solutions (1000 mg L^{-1}) of As(III), As(V), Cr(VI), Mo(VI), Sb(III), Sb(V), Se(IV), Se(VI) and V(V) were prepared from the following salts, respectively: $NaAsO_2$ (Fluka), $Na_2HAsO_4{\cdot}7H_2O$ (Merck), Na_2CrO_4 (Merck), $Na_2MoO_4{\cdot}2H_2O$ (Sigma), $KSbOC_4H_4O_6{\cdot}0.5H_2O$ (Merck), $KSb(OH)_6$ (Sigma), Na_2SeO_3 (Fluka), $Na_2SeO_4{\cdot}10H_2O$ (BDH) and Na_3VO_4 (Aldrich). Cr(III) solutions were prepared from a $Cr(NO_3)_3$ stock solution (1000 mg L^{-1}, Merck), and nitrate solutions from $Ca(NO_3)_2{\cdot}4H_2O$ (Merck). Single-element 1000 mg L^{-1} stock solutions of Al, Ca, Fe, K, Mg, Mn, Na and Sr (Spectrascan, Teknolab AS, Kolbotn, Norway) were used. All solutions were prepared in polyethylene containers and stored at 4 °C. Ultrapure water (18.2 MΩ cm, Millipore, Bedford, USA), Suprapur HNO_3 (65% m/m, Merck) and pro-analysis NaOH (Fluka) were used.

Three optimization solutions (I, II and III) were prepared with the following compositions: **I** – As(III), Sb(III) and Se(IV); **II** – As(V), Cr(VI), Mo(VI), Sb(V), Se(VI) and V(V) and **III** – Cr(III). The solutions were 10.0 μg L^{-1} with respect to each target element, unless stated. The pH of the solutions were adjusted with HNO_3 and NaOH.

2.4. Concrete sample and leaching procedure

The concrete material and the leaching procedure described in the previous study [1] were used. Leachates were prepared according to a standard pH-dependent leaching test [6] after crushing the concrete sample to <1 mm particle size. Leachants prepared by mixing deionised water with different volumes of 3.6 mol L^{-1} HNO_3 and 3.0 mol L^{-1} NaOH were used to generate leachates in the pH range 3.1–13.4. A leachate was also prepared without pH adjustments using deionised water resulting in a “natural pH” of 12.5. All the leachates were prepared at a liquid-to-solid ratio of 10. The electrochemical potential (Eh) of the leachates was measured as described in [10].

2.5. Optimum SPE procedures

As optimized previously [1], the Extract-Clean SAX was conditioned with 10.0 mL deionised water, acetate buffer, ammonia buffer and phosphate buffer to extract the anionic analytes from mildly acidic (pH 4–7), neutral (pH ∼ 7), mildly basic (pH 8–10) and strongly basic (pH 11–13) leachates, respectively. The buffer solutions had pH values close to those of the samples [1]. A leachate of pH ≥ 12.5 was extracted using one SAX tube, whereas a leachate prepared using acidified leachant (pH < 12.5) was successively passed through five SAX tubes. In both cases, 5.0 mL aliquot of the leachate was applied to the sorbent(s). The Bond Elut SCX was conditioned with 5.0 mL deionised water. A leachate (5.0 mL) of pH ≤ 5 was passed through three SCX cartridges, and a pH 5–10 leachate (5.0 mL) was applied to one SCX cartridge. In all extractions, the flow rate of the conditioning and the sample solutions was maintained at 5.0 mL min^{-1} using a peristaltic pump.

2.6. Quantification of analyte species

The analyte fractions retained on each ion-exchange sorbent were calculated as the difference in element concentration between the original sample and the SPE effluent. In the elution studies (Section 3.5) and in the analysis of the leachate samples (Section 4), the retained analyte species were eluted with 1.0 mol L^{-1} HNO_3 at a flow rate of 0.2 mL min^{-1} and determined.

3. Results and discussions

3.1. Optimization of the multiple anion-exchange SPE method

The retention of a charged species on an ion-exchanger is affected by the type and concentration of matrix ions which compete for the exchange site. Our previous study [1] found that the quantitative extraction of the anionic analytes from a 10.0 mL sample was not affected by the interference from NO_3^-, SO_4^{2-}, CO_3^{2-}, PO_4^{3-}, $Al(OH)_4^-$ and $Si(OH)_6^{2-}$ co-existing at individual ion concentration of up to 100 mg L^{-1}. However, very high concentration of NO_3^- affected the extraction of the target anions [7]. The leachate samples analysed in the present study contained up to 16 g L^{-1} NO_3^-.

Several ways are known to overcome interferences in SPE, including masking and precipitation of the interferent, diluting the sample, decreasing the sample volume and increasing the sorbent mass. As far as NO_3^- is concerned, suitable reagents are not available for its masking or precipitation. Sample dilution will affect the detectability and the species distribution of analytes. In the present study, experiments were carried out to see if repeated extractions of a sample solution could be used to overcome the interference from NO_3^-, and eventually to find out the number of extractions on identical tubes needed for quantitative retention of the analytes. The previously identified optimum extraction conditions were used, i.e. sorbent type (500 mg Extract-clean SAX), conditioning (buffer type, volume and flow rate), sample percolation rate and elution solvent [1]. Increasing the mass of the SAX was not practical in the present case because the material is commercially available only with sorbent masses in the range 100–1000 mg.

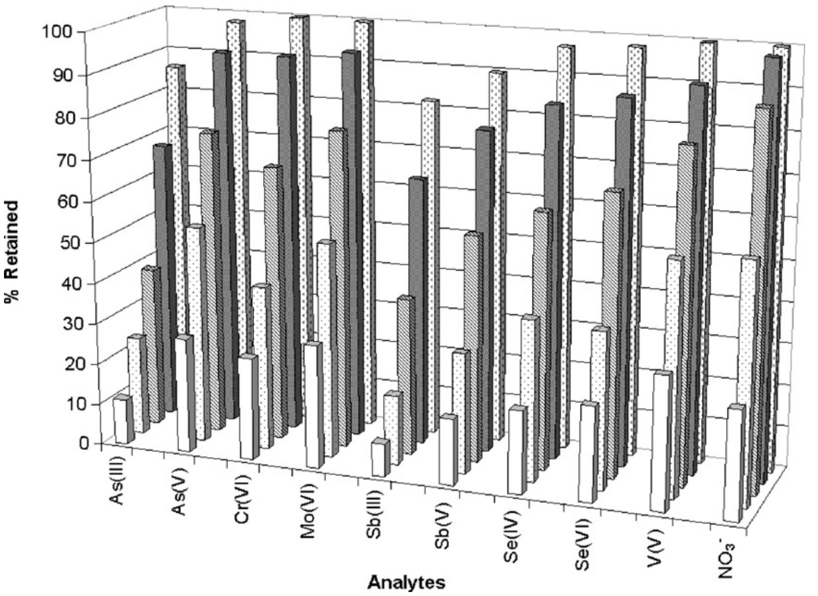

Fig. 1. Cumulative fractions of As, Cr, Mo, Sb, Se and V species and NO_3^- retained on Extract-Clean SAX sorbents in the multiple extractions of 5.0 mL multi-element standard solutions, pH 11 (solution I and II, see experimental part) containing 16 g L^{-1} NO_3^-. The results shown are the averages of two experiments. Extraction steps: 1 (□), 2 (⬚), 3 (▧), 4 (▩) and 5 (⬚).

In the optimization of the multiple SPE procedure, aliquots (5.0 mL) of solutions I and II (see Section 2.3) treated with 16 g L^{-1} NO_3^- and adjusted to pH 11 were separately passed through a series of SAX tubes conditioned with phosphate buffer (see Section 2.5). The 5.0 mL samples contained 80 mg (1.3 mequiv.) of NO_3^-. Fig. 1 presents the cumulative fractions of the species retained after each extraction step. 22–32% of the As(V), Cr(VI), Mo(VI), Se(IV), Se(VI) and V(V) were retained at the first extraction step and more than 85% of the species were retained at the fourth. Only 8–16% of the As(III), Sb(III) and Sb(V) were retained on the first SAX, and 65–80% on four sorbents; a fifth extraction step was therefore needed to improve their retention to 80–90%. Fig. 1 also shows the fractions of NO_3^- retained from solution II after each extraction step. Only 26% of the ion (0.34 mequiv.) was retained on the first SAX and cumulative retentions of 58, 89, 99 and 101% were obtained in the successive steps, respectively.

A closer look at the retention of NO_3^- across the multiple extraction steps shows that the SAX sorbents (capacity = 0.75 mequiv./500 mg) were not saturated by the NO_3^- at each extraction step, so the analytes, which are present at low concentrations, had the chance to interact with the ion-exchange sites. A series of experiments showed that, once retained, the analytes are not displaced by NO_3^- most likely due to their strong retention: attempts were made to elute the anionic species retained on the SAX from solutions I and II (see Section 2.3) with 16–62 g L^{-1} NO_3^- solutions, but none of the analytes were eluted. The different retention behavior of the analytes across the multiple extraction steps (see Fig. 1) is probably due to their different interaction with the anion-exchanger; ion-exchangers generally have better selectivity for ions of high charge and large ionic radius (low degree of hydration) [11].

3.2. Validation of the multiple anion-exchange SPE method

The multiple anion-exchange extraction method was validated addressing the effect of matrix constituents co-existing in concrete leachates. Leachate samples of pH 7.2 and 11.3, which originally contained 13 and 9 g L^{-1} NO_3^-, respectively, were divided into two portions (A and B) and spiked with 10.0 $\mu g\,L^{-1}$ of the following species just before extraction: A – As(III), Sb(III) and Se(IV), and B – As(V), Cr(VI), Mo(VI), Sb(V), Se(VI) and V(V). The SAX sorbents were conditioned with the suitable buffer (see Section 2.5), and the spiked leachates were passed through the sorbents at 5.0 mL min^{-1}. The spike recovery of As(III) (pK_a 9.3) [12] was evaluated from the pH 11.3 leachate. The multiple extraction of each of the spiked leachates (pH 7.2 and 11.3) through five SAX tubes gave 78–95% retention of the spiked analytes. The lower retentions found (78, 81 and 83%) were for Sb(III), As(III) and Sb(V), respectively. 95 and 97% of the NO_3^- were retained from the pH 7.2 and 11.3 leachates, respectively, after the fifth extraction steps. The pH of the effluents of the leachates from the fifth SAX was lowered from the original pH of the leachates by a maximum of 0.6 units.

The optimization results show that more than 90% of most of the trace anionic analytes can be extracted from leachates of very high interferent-to-analyte ratio by passing a small sample volume (5 mL) through up to five identical SAX tubes. If an SPE tube with a high sorbent mass is available, the number of repeated extractions may be decreased.

3.3. Optimization and validation of the cation-exchange SPE method

A cation-exchange SPE method was developed using a Bond Elut SCX sorbent which had a silica resin. Silica-based sorbents have the advantage over polymer-based sorbents that they do not need thorough conditioning [13,14]. The SCX sorbent was conditioned with 5.0 mL deionised water at a flow rate of 5.0 mL min^{-1}. A Cr(III) standard solution (solution III, see Section 2.3) was adjusted to pH 3.0 and 5.0, and aliquots (5.0 mL) of the solutions were passed through the SCX cartridges at 5.0 mL min^{-1}. Analysis of the SPE effluents of the solutions showed that more than 95% of the Cr(III) was retained at both pH values.

The cation-exchange extraction method was validated taking the effect of matrix constituents into account. Three concrete leachates of pH 3.1, 5.1 and 7.2 with respective Cr concentrations of 890, 2.2 and 11 $\mu g\,L^{-1}$ were spiked with 250, 10.0 and 10.0 $\mu g\,L^{-1}$ Cr(III), respectively. Aliquots (5.0 mL) of the leachates were passed through pre-conditioned SCX cartridges at 5.0 mL min^{-1}. It was found that the spike recovery of Cr(III) varied among the leachates. A single-step extraction of the solutions gave 47, 88 and 92% recov-

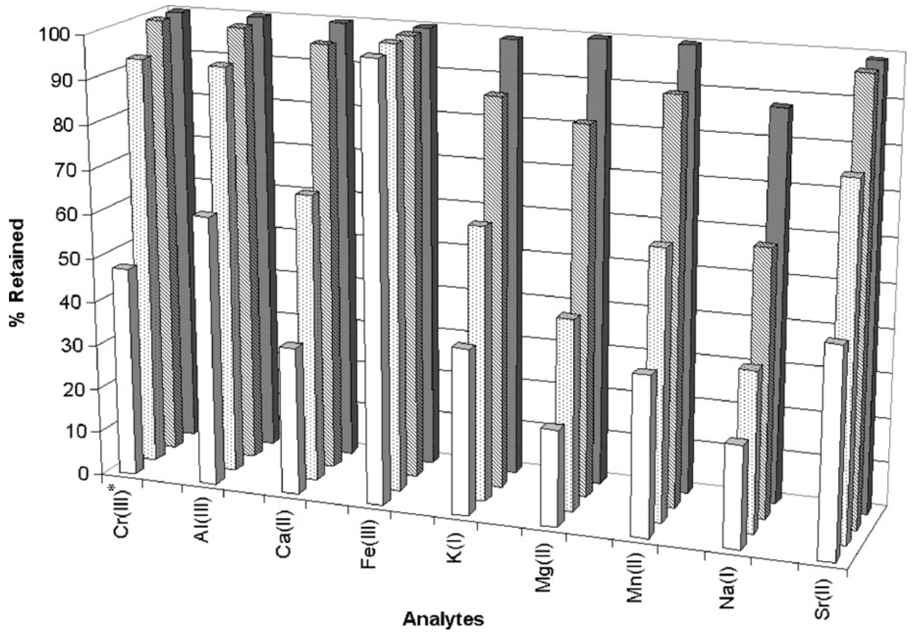

Fig. 2. Cumulative fractions of metal cations retained on the Bond Elut SCX sorbents in the multiple extractions of 5.0 mL aliquot of a pH 3.1 concrete leachate spiked with 250 μg/L Cr(III). See Table 1 for the concentrations of the metals in the leachate. The results shown are the averages of two experiments. Extraction steps: 1 (□), 2 (⬚), 3 (▨) and 4 (▩). *The retention of spiked Cr(III) was calculated as: $\frac{\text{analyte retained from the spiked sample} - \text{analyte retained from the original sample}}{\text{spiked amount}} \times 100$.

Table 1
Concentrations of metals in the pH 3.1 concrete leachate.

Metal cation	Al(III)	Ca(II)	Fe(III)	K(I)	Mg(II)	Mn(II)	Na(I)	Sr(II)
Concentration (mg L^{-1})	219	6385	6.5	46	129	4.6	8.1	6.1
Amount in 5.0 mL aliquot (mequiv.)[a]	0.014	0.4	1.9×10^{-4}	6×10^{-3}	0.013	2×10^{-4}	0.002	1.8×10^{-4}

[a] 5.0 mL aliquot of the leachate was successively passed through SCX cartridges.

ery of the spiked analyte from the pH 3.1, 5.1 and 7.2 leachates, respectively. The low recovery of Cr(III) from the pH 3.1 leachate could be due to the simultaneous retention of matrix cations; relatively high amounts of metal cations are leached from cement-based materials under strongly acidic conditions [15]. The leachate was successively passed through a series of SCX cartridges: 99% recovery was achieved for the spiked Cr(III) at the third step, see Fig. 2. In the multiple extraction of the pH 3.1 leachate, the retention of other metal cations existing at high concentrations (see Table 1) was also monitored. As shown in Fig. 2, all the metals were retained along with Cr(III) as proved by their very low concentration in the last effluent. The pH of the acidic leachate (pH 3.1) effluent reached 1.7 after the fourth extraction step; this was probably caused by the counter-ions of the SCX (H^+) released to the solution in the cation-exchange process.

3.4. Non-specific adsorption of analytes on the ion-exchange sorbents

In ion-exchange extractions, mechanisms other than electrostatic attractions may contribute to the retention of substances on the sorbent. Such adsorption effects should be evaluated, especially in multiple extraction procedures, as they may introduce significant error. The behaviour of the anionic and cationic analyte species on the SCX and SAX sorbents, respectively, was examined as follows. Standard solutions of the anionic analytes (solution I and II, see Section 2.3) were adjusted to pH 4, 7 and 10, and aliquots (5.0 mL) of each of the solutions were subsequently passed through three SCX cartridges. Analysis of the effluents from the third SCX showed that 92–97% of all the anionic species passed through the sorbents with the exception of V(V) for which only 13 and 26% passed at pH 4 and 7, respectively.

In a similar way, the behaviour of Cr(III) on the SAX sorbent was examined using solution III (see Section 2.3) adjusted to pH 3 and 5. Aliquots (5.0 mL) of each solution were successively passed through five SAX tubes. Analysis of the effluent from the fifth SAX showed that 91 and 94% of the Cr(III) in the two solutions, respectively, passed through the five SAX sorbents.

3.5. Elution of the retained analytes

It was demonstrated, in our previous study [1], that the anionic species of the target elements can be quantitatively eluted from the SAX sorbent using HNO_3 solution. HNO_3 can also be used to elute cations from SCX sorbents as H^+ ion neutralizes the cation-exchange sites thereby desorbing the retained species. In addition, in strongly acidic conditions ($pH < 2$), the covalent bonds linking the silica resin and the ion-exchange functionality are destabilized, facilitating the release of analytes from the sorbent. For the present multiple anion- and cation-exchange extractions, a procedure was optimized for the elution of the analytes from each ion-exchange sorbent using small volumes of 1.0 mol L^{-1} HNO_3.

The anionic analyte species were extracted from solution I and II (see Section 2.3) treated with 16 g L^{-1} NO_3^- and adjusted to pH 11. Aliquots (5.0 mL) of each of the solutions were passed through five SAX tubes, and the analytes retained on each SAX were eluted with 1.0 mL of 1.0 mol L^{-1} HNO_3. The eluates from the five sorbents were mixed together and analyzed. The Cr(III) retained on three SCX sorbents from a 5.0 mL standard solution (solution III, see Section 2.3) was eluted and analyzed following a similar procedure. The

Table 2
Percentage of the anionic and cationic analytes eluted from the SAX and SCX sorbents, respectively.

% Eluted									
As(III)	As(V)	Cr(VI)	Mo(VI)	Sb(III)	Sb(V)	Se(IV)	Se(VI)	V(V)	Cr(III)[a]
108	94	94	96	105	107	98	96	92	95

After the multiple extraction of 5.0 mL of a standard solution (solution I, II or III, see Section 2.3), 1.0 mL of 1.0 mol L^{-1} HNO_3 was passed through each SPE tube at 0.2 mL min^{-1}. Eluates of each extraction step were mixed together and analyzed. The results are the averages of two experiments.

[a] Cationic analyte.

eluents were passed through the SAX and SCX sorbents at a slow rate (0.2 mL min^{-1}) to provide adequate contact time between the solvent and the retained analytes (or the sorbent). As can be seen from Table 2, the elution procedure gave 92–108% recovery for the analyte species.

4. Fractionation analysis of the target elements in leachates from a concrete material

The leaching of As, Cr, Mo, Sb, Se and V from a concrete material (see Section 2.4) in the pH range 3.8–13.4, and the fractions of the elements retained on SAX and SCX sorbents from the leachates are presented in Fig. 3. The anionic and cationic fractions of the target elements in the leachates prepared from acidified leachants (i.e. the pH 3.8–11.3 leachates) were determined using the multiple extraction procedures developed in the present study. The previously optimized single-step anion-exchange SPE [1] was used to determine the anionic fractions in the leachates prepared without acidifying the leachant (pH 12.5 and 13.4, see Fig. 3). The concentrations of the anionic and cationic analytes were calculated as the difference in element concentration between a leachate and the SAX and SCX effluent, respectively. The retained species were also eluted with 1.0 mol L^{-1} HNO_3 and determined; the elution results were in the range 89–112% of those presented in Fig. 3. The cation-exchange extraction results for V are not included due to the non-specific adsorption of V(V) on the SCX (Section 3.4).

The release patterns of the target elements (total concentration), which can be seen from Fig. 3, are similar to the previously found results for a similar concrete material [1]. Most of the elements have maximum solubility in the mildly alkaline and neutral regions, and a decrease in concentration was observed for the elements in the mildly acidic leachates. The charge-based fractionation analysis results in the figure show that the target elements predominantly existed as anions in the “natural pH” and the strongly alkaline leachates (pH 12.5 and 13.4, respectively). These results are similar to those obtained previously [1], but in addition the present study identified high fractions of anions also in the leachates of pH 7.2–11.3 (As, Cr, Se and V), pH 3.8–11.3 (Mo) and pH 8.2–11.3 (Sb).

In cement matrix, the oxyanionic species of the target elements are incorporated in the structures [5,16–19] and sorb onto the surfaces [5,19] of cement hydrate phases. Some of the oxyanions also precipitate as metalates [5,16]. The anionic species of the target elements predominated in the above-listed alkaline and neutral leachates because the hydrated cement phases, that are stable in strongly alkaline regions, start to degrade as the pH of the cement material is lowered [20] releasing the oxyanions from their structures into the leaching solution. A rough assessment of the stability of the element species in the leachates based on the measured pH and Eh values (see Fig. 3) in conjunction with the stability diagrams of the elements [21] indicates that the oxyanionic species of most of the elements are likely to be stable at the pH-Eh conditions of the leachates. More precise information about the stability of the element species in the leachates may be obtained by constructing pH-Eh diagrams for the leachates under consideration. As Cornelis et al. [5] explained (see also the references therein), the lower concentrations of the target elements in the mildly acidic leachates may be due to the sorption of the released oxyanionic species onto the surfaces of amorphous Al and Fe oxides, which start to develop positive charge in the acidic ranges. In addition, some of the oxyanions may precipitate as metalates.

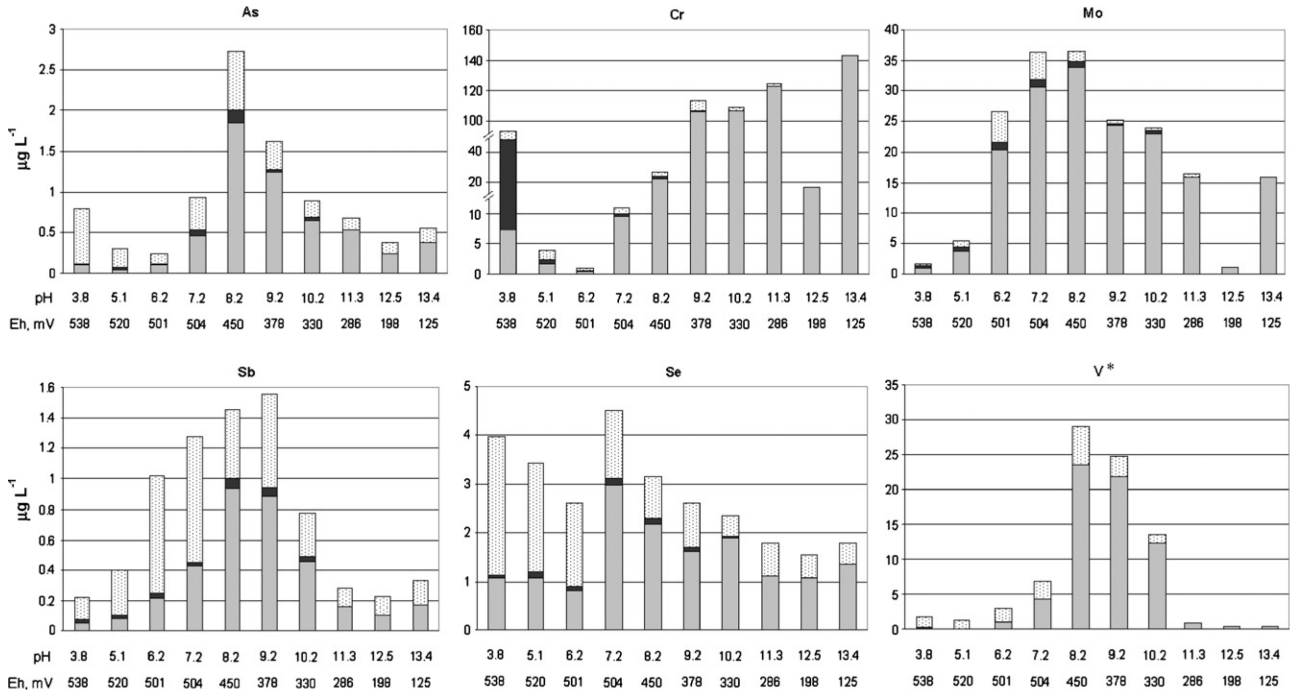

Fig. 3. Total concentrations (µg L^{-1}) and fractions of As, Cr, Mo, Sb, Se and V retained on the SAX and SCX sorbents from concrete leachates of pH 3.8–13.4. The pH 12.5 leachate was prepared using deionised water (without acid/base addition). Shadings: element fractions retained on the anion (▢) and cation (■) exchangers. (▨) represents the fraction of elements not retained on the ion-exchangers. *The cation-exchange extraction results for V are not included due to non-specific adsorption of V(V) on the SCX.

The fractionation analysis of the elements based on cation-exchange extraction showed that very small fractions of the elements were retained on the SCX sorbents from most of the leachates cationic species of the target elements do not exist in the leachates, except for Cr at pH 3.8 (see Fig. 3). The retention of small fractions of the elements on the SCX might be due to their non-specific adsorption; up to 8% adsorption was observed for the anionic species on the SCX (see Section 3.4). More than 85% Cr was retained on the SCX from the acidic leachate (pH 3.8), indicating that Cr(III) may be released at low pH due to the dissolution of mineral phases which bound it.

5. Conclusions

This study has demonstrated the use of multiple extractions to overcome matrix interferences in the fractionation analysis of As, Cr, Mo, Sb, Se and V species in leachates from cement-based materials using ion-exchange SPE. In the multiple extractions, a small volume of a leachate was percolated through a series of identical ion-exchange sorbents. It is shown that the interference from NO_3^- in the anion-exchange SPE can be overcome by passing the sample aliquot through five pre-conditioned SAX sorbents. Similarly, the extraction of Cr(III) from leachates containing a high concentration of metal cations can be improved by passing the sample through three SCX sorbents. Single-step extractions were sufficient to extract the anionic and cationic analyte species from leachates having low concentration of matrix ions. The SPE methods were used to fractionate the anionic and cationic species of the target elements in leachates prepared in the pH range 3.8–13.4. Compared to the total element concentrations usually reported, the results of this study provide more information concerning the pH-dependent release mechanism(s) of the elements, and the stability of the species in the leachates. The ion-exchange SPE methods should also be suitable for the fractionation analysis of elements in other samples of complex matrix composition (with some procedural adjustments, if required). If SAX and SCX tubes with high sorbent masses are available, the number of repeated extractions may be decreased.

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