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Simultaneous speciation of chromate, arsenate, molybdate and vanadate in alkaline samples by HPLC–ICP-MS at different concentration levels of vanadate†

Ana Drinčić, [ID] [ab] Janez Ščančar, [ID] [ab] Tea Zuliani, [ID] [ab] Irena Nikolić [ID] [c] and Radmila Milačič [ID] *[ab]

Flay ash, cement and electric arc furnace (EAF) dust are frequently mixed in building composites. From them, chromium (Cr), arsenic (As), molybdenum (Mo) and vanadium (V) may be leached. Concentrations of V in leachates may be significantly higher than those of Cr, As and Mo, making simultaneous speciation analysis particularly difficult. In this work, a high performance liquid chromatography inductively coupled plasma mass spectrometry (HPLC–ICP-MS) procedure was used for simultaneous speciation of chromate, arsenate, molybdate and vanadate. First, the behaviour of Cr, As, Mo and V species in different oxidation states was studied during their separation under acidic (pH 5) and alkaline (pH 12) conditions. At alkaline pHs chromate, arsenate, molybdate and vanadate were simultaneously separated and eluted at retention times from 390 to 450 s, 230 to 270 s, 340 to 430 s and 270 to 380 s, respectively and detected on-line by ICP-MS, recording m/z 52, 75, 95 and 51, respectively. When V species were leached in significantly higher concentrations than Cr, Mo and As, their detection was possible at the low abundance (0.25%) ^{50}V isotope, which is also the mass of the ^{50}Cr isotope (abundance 4.345%), due to selective separation between V and Cr species. Good repeatability of measurement (RSD better than ±3.0%) and quantitative elution of elemental species (column recoveries 99–105%) were obtained. Finally, the procedure was applied in the simultaneous speciation analysis of chromate, arsenate, molybdate and vanadate in highly alkaline aqueous leachates from composites consisting of fly ash, cement and EAF dust that contained a wide range of concentrations of vanadate.

1. Introduction

High performance liquid chromatography (HPLC) coupled to an inductively coupled plasma mass spectrometry (ICP-MS) detector is a powerful tool for the elemental speciation analysis in a variety of environmental and biological samples.[1–3] Despite the possibility of multielemental detection, speciation analysis by HPLC-ICP-MS is usually carried out separately for the species of a particular element. Simultaneous speciation analysis of two or more elements is possible only if the chemical species of different elements behave similarly during the analysis. Multielemental speciation analysis, which is scarcely documented, requires such chromatographic conditions that enable selective separation and quantitative elution of all

elemental species of interest. Morita *et al.*,[4] for example, developed a sensitive method for the simultaneous speciation of arsenic (As) and antimony (Sb) in hot spring water and fish samples by HPLC-ICP-MS. By the use of a C30 reversed phase column and careful optimization of the chromatographic conditions, it was possible to separate eight As (As(III), As(v), monomethylarsonic acid (MMAA), dimethylarsinic acid (DMAA), arsenobetaine (AB), arsenocholine (AsC), trimethylarsine oxide (TMAO) and tetramethylarsonium (TeMA)) and two antimony species (Sb(III) and Sb(v)). Bednar *et al.*[5] performed separation of oxoanions of tungsten (W), molybdenum (Mo) and phosphorus (P) on an anion-exchange Dionex AS-11 chromatographic column. Coupling of this column to ICP-MS enabled simultaneous speciation analysis of tungstate, molybdate, and phosphate at the sub µg L^{-1} concentration levels in ground water and aqueous soil extracts. Wolf *et al.*[6] modified the analytical method that was previously developed for the determination of Cr(III) and Cr(vi) by HPLC-ICP-MS. The usage of a silica based Brownlee C8 column and the same chromatographic conditions as for the Cr speciation allowed the simultaneous determination of As(III), As(v), Se(iv), Se(vi), Cr(III),

[a]Department of Environmental Sciences, Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia. E-mail: radmila.milacic@ijs.si; Tel: +386 1 4773560
[b]Jožef Stefan International Postgraduate School, Jamova 39, 1000 Ljubljana, Slovenia
[c]University of Montenegro, Faculty of Metallurgy and Technology, Džordža Vašingtona bb, 81000 Podgorica, Montenegro

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and Cr(VI) in leachates from ash and soil affected by wildfires. Simultaneous speciation analysis of As, Sb and thallium (Tl) species (As(III), As(V), Sb(III), Sb(V), Tl(I), and Tl(III)) in river water samples was reported in which an anion-exchange Dionex IonPac AS-7 column coupled to ICP-MS was used.[7] The analytical procedure was also optimized for the simultaneous speciation of As(III), As(V), monomethylarsenic acid (MMA), dimethylarsenic acid (DMA), Cr(III) and Cr(VI), and Cd(II) in water samples on an anion-exchange Hamilton PRP-X100 column with ICP-MS detection.[8] In our group, a method developed for the determination of Cr(VI) in different sample matrices by anion-exchange HPLC-ICP-MS[9–12] was modified and adapted so that it was possible to simultaneously determine concentrations of chromate, molybdate, tungstate and vanadate in welding fume extracts.[13]

It is important to stress that chromatographic conditions for the multielemental speciation analysis must be optimized so that chemical species of a given element are selectively separated on a stationary phase and quantitatively eluted from the column, while there is no need for selective separation of species of different elements, as long as their m/z ratios monitored by ICP-MS do not overlap. At the same time, it is desired that chemical species of the elements analysed are present at similar concentration levels. However, this is not always the case when real environmental samples like leachates from building composites are analysed. Re-use of industrial waste by-products in different building materials is an acceptable alternative in waste management,[14–16] only if such materials possess appropriate technical characteristics[17] and their use is environmentally safe.[6] For evaluation of the release of toxic substances from building composites, different leaching tests are applied,[18–20] using mainly demineralised water as the leaching solution. Although speciation is of crucial importance for the estimation of elemental toxicity and mobility,[1–3] information on the extent of leaching of chemical species of elements from the re-cycled building materials is still scarce and was mainly focused on speciation of Cr in aqueous samples from different leachability tests.[17,19,21–23] Among pollutants in wastes from thermal power plants and steel-making industry, Cr, As, Mo and vanadium (V) are usually present in concentrations of environmental concern.[20] In our group, environmental impacts of building composites, which were 98% composed of a mixture of fly ash (80%) and cement (20%), with the remaining 2% being electric arc furnace (EAF) dust, were evaluated by the use of leachability tests over a period of 6 months.[20] Due to the presence of Ca(OH)$_2$ and CaCO$_3$, the aqueous leachates were highly alkaline. Hence, the HPLC-ICP-MS procedure, already used in the analysis of welding fume alkaline extracts, was successfully applied for the simultaneous determination of chromate, molybdate and vanadate.[13] This study revealed that in the first 4 days after the start of the experiment, chromate, molybdate and vanadate were leached in comparable amounts, while after 9 days, more intensive leaching of vanadate, in amounts 20 to 30 times higher than those of chromate and molybdate, was observed, making simultaneous speciation analysis very difficult. Therefore, in leachates that contained high V concentrations, speciation

analysis of V was carried out separately in additionally diluted samples. The experimental data also showed that As was leached in relatively high concentrations. Consequently, As speciation was needed for the evaluation of its environmental impacts.

In the present work, novel approaches to the simultaneous speciation analysis of Cr, As, Mo and V by HPLC-ICP-MS, using an anion-exchange Mono Q column in real world samples, were investigated. Separated elemental species were monitored at m/z 52, 75 and 95, for Cr, As and Mo, respectively, while for V species at m/z 51 and 50. Chromatographic conditions were optimized so that selective separation of V and Cr species was achieved, enabling detection of high concentrations of V at its low abundance (0.25% (ref. 24)) ^{50}V isotope, which is also the mass of the ^{50}Cr isotope (abundance 4.345% (ref. 24)). Once developed and optimized, the analytical procedure was applied in the simultaneous speciation analysis of chromate, arsenate, molybdate and vanadate in highly alkaline samples of aqueous leachates from building composites, which were made up of various mixtures of fly ash, cement and EAF dust and were left in the leaching solution for different times.

2. Experimental

2.1. Instrumentation

Concentrations of elements were determined by ICP-MS on an Agilent (Tokyo, Japan) 7900 instrument. Chromatographic separations of elemental species were performed on an Agilent series 1200 quaternary pump equipped with a model 7725i Rheodyne sample injection valve (Cotati, CA, USA) fitted with a 0.2 mL injection loop. For the separation of Cr, As, Mo and V species a strong anion-exchange fast protein liquid chromatography (FPLC) column, Mono Q HR 5/5 (GE Healthcare Bio-Sciences, Uppsala, Sweden) (column dimensions 5 × 50 mm, matrix polystyrene/divinyl benzene, pH stability 2–12, particle size 10 μm) was used. The outlet of the chromatographic column was directly connected to the Miramist nebuliser and Scott-type spray chamber of the ICP-MS instrument. Nickel sampler and skimmer cones were used with 1.0 and 0.4 mm orifices, respectively. To control the stability of the mass spectrometer, the eluent was spiked (post-column addition) with internal standards of 100 μg L^{-1} germanium (Ge), scandium (Sc), rhodium (Rh) and indium (In). Data were treated with Agilent MassHunter software. Data processing was based on the peak area. Experimental working conditions for ICP-MS were optimized for plasma robustness and adequate sensitivity using a high matrix introduction (HMI) system. Samples analysed contained high amounts of carbonates and sulphur compounds, while NaCl that was used as the eluent in the chromatographic separation contained chloride ions, which contribute to the formation of polyatomic interferences. To eliminate severe polyatomic interferences of ^{34}S^{16}O$^+$ at m/z 50, ^{34}S^{16}O^{1}H$^+$, ^{35}Cl^{16}O$^+$ and ^{38}Ar^{13}C$^+$ at m/z 51, ^{35}Cl^{16}O^{1}H$^+$, ^{40}Ar^{12}C$^+$ and ^{34}S^{18}O$^+$ at m/z 52 and ^{40}Ar^{35}Cl$^+$ at m/z 75,[25] high energy collision mode (HECM) was applied.[9] The use of HMI reduced the sample aerosol transport, and enabled direct analysis of separated elemental species in the presence of up to 1 mol L^{-1}

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J. Anal. At. Spectrom., 2017, **32**, 2200–2209 | **2201**

of NaCl.[9] ICP-MS operating parameters are summarized in Table S1 (ESI†).

A WTW 330 pH meter (WTW GmbH, Weilheim, Germany) was employed to determine the pH.

A Mettler AE 163 (Mettler Toledo, Zürich, Switzerland) analytical balance was used for weighing.

2.2. Reagents and materials

All solutions were made up using ultrapure 18.2 MΩ cm water (MilliQ) obtained from a Direct-Q 5 Ultrapure water system (Millipore Watertown, MA, USA). Suprapur sodium hydroxide monohydrate ($NaOH \cdot H_2O$) and Suprapur sodium carbonate (Na_2CO_3) from Merck (Darmstadt, Germany) were used for the preparation of alkaline buffer solutions (2% NaOH + 3% sodium carbonate Na_2CO_3) and ultrapure hydrochloric acid (HCl) to adjust the pH of standard solutions applied in speciation analysis. As a reducing agent, anhydrous sodium sulphite (Na_2SO_3) from Acros Organics (Geel, Belgium) was used. Stock standard solutions of Cr, As, V, Ge, Sc, In and Rh (1000 ± 2 mg L^{-1} in 2–3% HNO_3) were purchased from Merck. Chromate was prepared from a stock solution of K_2CrO_4 in water (Merck), containing 1000 ± 2 µg mL^{-1} of CrO_4^{2-} and molybdate from a stock solution of $(NH_4)_6Mo_7O_{24}$ in water (Merck), containing 1000 ± 2 µg mL^{-1} of Mo. Arsenate and arsenite stock solutions (1000 ± 2 µg As mL^{-1}) were made by dissolving 0.4170 g of $Na_2HAsO_4 \cdot 7H_2O$ salt (Sigma-Aldrich, St Louis, MO, USA) in 100 mL of water and by appropriate dilution of 0.05 mol L^{-1} $NaAsO_2$ (Sigma-Aldrich) with water, respectively, while for the preparation of vanadate stock solution, 0.2296 g of NH_4VO_3 p.a. salt (Merck) was dissolved in 100 mL of alkaline buffer to obtain a solution containing 1000 ± 2 µg V mL^{-1}. Sodium chloride of suprapur quality (Merck) was used in HPLC separations.

2.3. Preparation of working standard solutions

To follow the behaviour of chromate, arsenate, molybdate and vanadate on a HPLC column with ICP-MS detection, working standard solutions were prepared daily by the appropriate dilution of stock standard solutions at pH of 5 (adjusted with 0.0006 mol L^{-1} HCl) and at pH of 12 (using buffer solution composed of 0.2% NaOH + 0.3% Na_2CO_3). For examining the efficacy of the analytical procedure to separate species of individual elements in their highest and lower oxidation states, Cr(III) and As(III) standard solutions were used. For preparing Mo and V species in their lower oxidation states, 1 mL of Na_2SO_3 solution (0.004 g mL^{-1} and 0.002 g L^{-1}, respectively) was added to molybdate and vanadate working standard solutions and the contents were diluted to 10 mL.

2.4. Preparation of building composites from fly ash, cement and electric arc furnace dust

Building composites were prepared from fly ash and EAF dust obtained from the coal-fired power station Pljevlja and the steel-mill Nikšić in Montenegro, and portland cement CEM II/B-M(S-LL) 42.5 N. They were composed of 99.5% mixture of fly ash (70%) and cement (30%) and 0.5% EAF dust, 99.5% mixture of fly ash (80%) and cement (20%) and 0.5% EAF dust, 100%

mixture of fly ash (70%) and cement (30%), and 98% mixture of fly ash (80%) and cement (20%) and 2% EAF dust. The composite casts were cylinders, 7 cm in height and 5 cm in diameter, with a volume of approximately 0.137 L. The composites were immersed into MilliQ water and leachates taken 1 day or 9 months after the start of the experiment.

2.5. Speciation procedure

The separation procedure that was originally developed and validated for speciation of Cr(VI) by HPLC-ICP-MS was applied.[9] 0.2 mL of the sample was injected onto the column. To reduce the blank arising from the stainless steel needle, the sample was drawn with the syringe in the opposite direction through the plastic tube of the waste exit from the injector (reverse injection).[9] Linear gradient elution from water to 0.7 M NaCl (0–100%) was applied for 10 min at a flow rate of 1.5 mL min^{-1}. The eluate from the column was connected on-line to the ICP-MS. After separation, the column was regenerated with 2 mol L^{-1} NaCl for 3 min and equilibrated with water for 7 min. The eluate from the regeneration step was directed to waste through a software controlled six-port valve. The stability and robustness of the chromatographic column in the pH range 2 to 12 enabled analysis of acidic (pH 5) and highly alkaline (pH 12) samples. Cleaning of the Mono Q column was performed after each set of experiments when the pH of the samples investigated was changed. For cleaning, 0.5 mL of 1 mol L^{-1} sodium hydroxide was injected onto the column resin and the chromatographic procedure applied. The cleaning procedure was repeated twice. Before each new series of experiments, two blank samples were first injected.[9]

At a pH of 12, the procedure enabled separation of chromate, arsenate, molybdate and vanadate in a single chromatographic run from 390 to 450 s, 230 to 270 s, 340 to 430 s and 270 to 380 s, respectively. Separated elemental species were detected on-line by ICP-MS, recording Cr, As, Mo and V at m/z 52, 75, 95 and 51, respectively. When V in the sample was present in significantly higher concentrations than Cr, Mo, and As, its signal was recorded at m/z 50.

If not stated otherwise, all the analyses were done at least in two replicates.

3. Results and discussion

3.1. Separation of chromium, arsenic, molybdenum and vanadium species on the HPLC column followed by ICP-MS detection

Properties of elements, like toxicity towards living organisms, behaviour and fate in the environment, *etc.* depend primarily on the chemical forms in which they are present in a given environment. Cr, Mo and V are more toxic in their highest oxidation states (Cr(VI), Mo(VI) and V(V), respectively), while As(V) is less toxic than As(III).[26–29] Oxoanions of Cr(VI), As(V), Mo(VI) and V(V) are highly mobile in the form of alkali chromates, arsenates, molybdates and vanadates and can be present in leachates from building composites of fly ash, cement and EAF dust. To reduce the time and cost of analysis, the applicability of the HPLC-ICP-

2202 | *J. Anal. At. Spectrom.*, 2017, **32**, 2200–2209

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MS procedure was investigated for the simultaneous speciation of chromate, arsenate, molybdate and vanadate in highly alkaline leachate samples. First, the behaviour of single elemental species in their highest and lower oxidation states was examined on an anion-exchange HPLC column applying the speciation procedure as described in Section 2.5. The study was performed using working standard solutions containing 20 ng mL^{-1} of a particular elemental species, prepared at pH 5 and 12 (see Section 2.3). The results are presented in Fig. 1–4.

For the study of Cr speciation (Fig. 1), aqueous standard solutions of chromate and Cr(III)-nitrate were used. In aqueous solutions more acidic than pH 5, Cr(III) exists mainly as the positively charged $Cr(H_2O)_6^{3+}$ complex, while Cr(VI) as the negatively charged $Cr_2O_7^{2-}$ species. At pH 12, Cr(III) is mainly present in the form of sparingly soluble $Cr(OH)_3$, and to a smaller extent also as the soluble $Cr(OH)_4^-$ complex, whereas Cr(VI) exists as the CrO_4^{2-} species.[30] Data from Fig. 1A show that Cr(III) at pH 5 is eluted with a solvent front, while Cr(VI) from 430 to 490 s (Fig. 1B). At pH 12, Cr(III) is mostly precipitated as $Cr(OH)_3$, which is strongly adsorbed on the column resin, while a small peak that eluted from 220 to 240 s corresponds to the $Cr(OH)_4^-$ complex (Fig. 1C). Cr(VI) is eluted from 390 to 450 s (Fig. 1D), and is separated from Cr(III) species. The small peak of the blank solution, which corresponds to Cr(VI) (Fig. 1C and D) arises from the alkaline buffer solution, in which Cr(III) and Cr(VI) standards were prepared at pH 12.

For the investigation of As speciation (Fig. 2), aqueous standard solutions of arsenite (As(III)) and arsenate (As(V)) were used. At a pH of 5, As(III) is present as H_3AsO_3 and As(V) as $H_2AsO_4^-$ species.[31] The data in Fig. 2A and B indicate that in acidic solutions As(III) and As(V) species are well separated. At pH 12 As(III) exists mainly as $As(OH)_3$,[32] and to a smaller extent as soluble $HAsO_3^{2-}$ and AsO_3^{3-} species.[31] At highly alkaline pHs, the only As(V) species is AsO_4^{3-}.[31] The data in Fig. 2C show that

$As(OH)_3$ is strongly adsorbed on the column resin, while $HAsO_3^{2-}$ and AsO^{3-} As(III) species are eluted as two small peaks from 50 to 150 s. From Fig. 2D it can be seen that As(V) species is eluted as a sharp peak from 230 to 270 s and is separated from As(III).

Investigation of Mo speciation at pH 5 and 12 is presented in Fig. 3. From acidic to alkaline pHs Mo(VI) prevails as MoO_4^{2-} species.[33] In lower oxidation states, Mo species are in aqueous solutions and stable only at acidic pHs, in the form of the positively charged trivalent $Mo(H_2O)_6^{3+}$, tetravalent $Mo_3O_4^{4+}$ and pentavalent $Mo_2O_4^{2+}$ complexes.[34,35] The aqua monomeric trivalent, tetravalent and pentavalent Mo species tend to polymerise, forming di- or trinuclear oxo Mo species.[35] In the study of Mo(VI) speciation, molybdate standard solution was used. Mo compounds in lower oxidation states are not soluble in water and can be dissolved by alkaline digestion, which induces oxidation to Mo(VI), and thus changes the speciation. To prepare Mo species in the lower oxidation states, Na_2SO_3 was added as a reducing agent to a standard solution of molybdate and the pH adjusted to 5 and 12. This reducing agent was chosen since it is present in the samples of alkaline leachates from fly ash, EAF dust and cement.[20] The results of these experiments are presented in Fig. 3. As can be seen from Fig. 3A, at pH 5 the monomeric Mo species formed after the reduction of Mo(VI) are eluted with the solvent front, while polymeric Mo(V), Mo(IV) and Mo(III) species are adsorbed on the column resin. Mo(VI) is eluted from 330 to 420 s (Fig. 3B) and is separated from species in lower oxidation states. At pH 12, the separated Mo(VI) species are eluted from 340 to 430 s (Fig. 3C and D). The addition of the reducing agent (0.0004 g mL^{-1} Na_2SO_3) to Mo(VI) solution resulted in 20% decrease of the Mo chromatographic signal. Reduced Mo species were adsorbed on the column resin and were separated from Mo(VI). A peak of the blank solution at pH 12, which represents about 12% of the analytical signal of
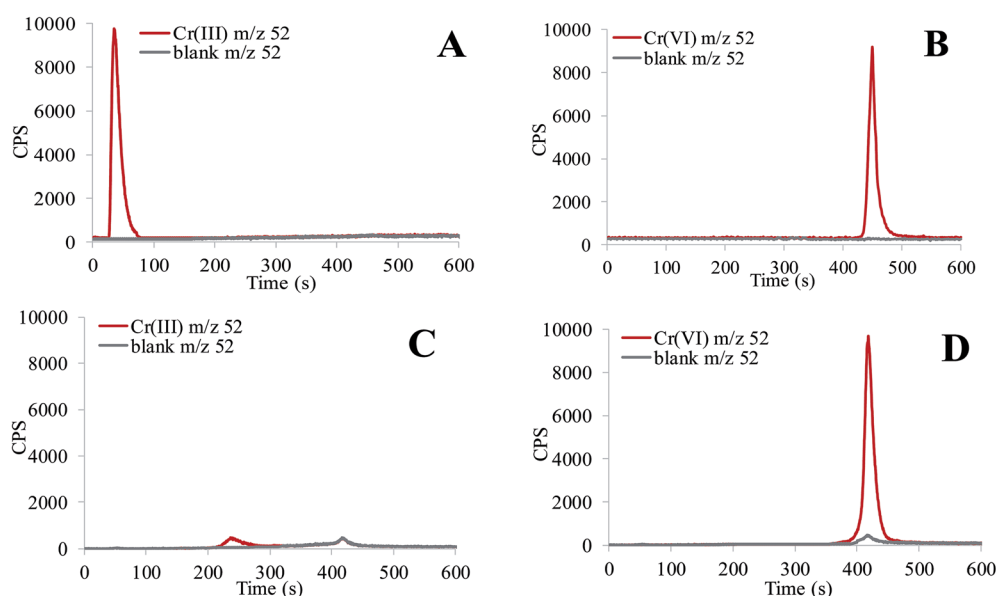

Fig. 1 Separation of (A) Cr(III) solution (pH 5), (B) Cr(VI) solution (pH 5), (C) Cr(III) solution in 0.2% NaOH + 0.3% Na_2CO_3 buffer (pH 12) and (D) Cr(VI) solution in 0.2% NaOH + 0.3% Na_2CO_3 buffer (pH 12) applying the HPLC-ICP-MS procedure (20 ng mL^{-1} of Cr).

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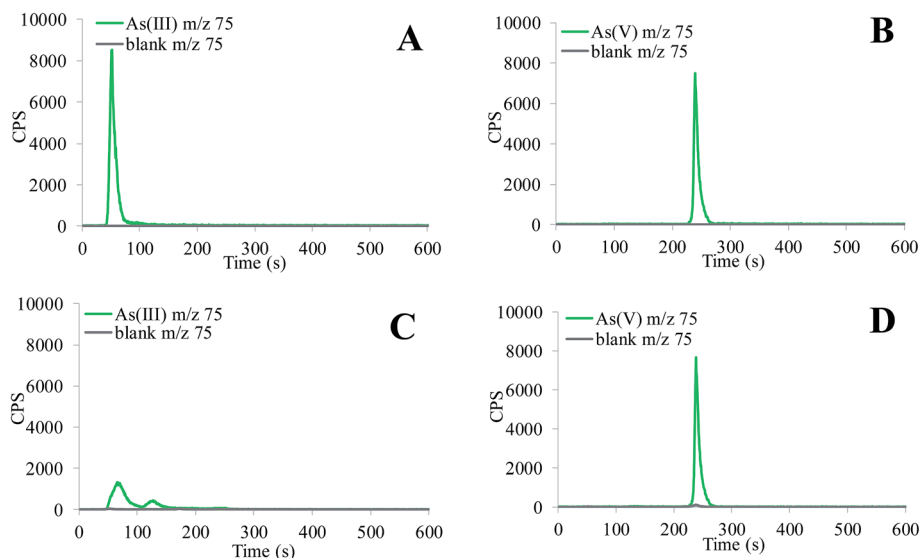J. Anal. At. Spectrom., 2017, 32, 2200–2209 | 2203

Fig. 2   Separation of (A) As(III) solution (pH 5), (B) As(v) solution (pH 5), (C) As(III) solution in 0.2% NaOH + 0.3% Na$_2$CO$_3$ buffer (pH 12) and (D) As(v) solution in 0.2% NaOH + 0.3% Na$_2$CO$_3$ buffer (pH 12) applying the HPLC-ICP-MS procedure (20 ng mL^{-1} of As).

Mo(VI), arises mainly from the metallic parts of the HPLC and injector and to a smaller extent also from the alkaline extract.

The study of V speciation at pH 5 and 12 is presented in Fig. 4. In aqueous solutions with acidic pHs, H$_2$VO$_4^-$ is a prevailing pentavalent monomeric V species,[36–38] which co-exists with the polyoxovanadate V$_4$O$_{12}^{4-}$ and HV$_{10}$O$_{28}^{5-}$ ions. The latter decavanadate anion is the predominant polymeric V species in the pH range between 3 and 6.[38,39] At pH 12, VO$_4^{3-}$ species prevails.[36–38] The main V species in lower oxidation states in aqueous solutions are tetravalent VOOH$^+$ and VO^{2+}, and trivalent V(H$_2$O)$_6^{3+}$ aqua complex and VOH$^+$ species, which are stable at acidic pHs.[36,37] Since tetravalent and trivalent V

compounds are sparingly soluble in water, Na$_2$SO$_3$ (0.0002 g mL^{-1}) was added as a reducing agent to a standard solution of vanadate to prepare the V species in the lower oxidation states. Then the pH was adjusted to 5 and 12. From data presented in Fig. 4A and B it can be seen that at pH 5, V(v) is separated from V species in the lower oxidation states. The positively charged V complexes formed after the reduction of V(v) are eluted with the solvent front, whereas negatively charged pentavalent polyoxovanadate complexes are eluted as a broad peak from 300 to 600 s. At pH 12, the pentavalent VO$_4^{3-}$ species is eluted from 270 to 380 s (Fig. 4D). The addition of a reducing agent to V(v) solution resulted in about 50% decrease
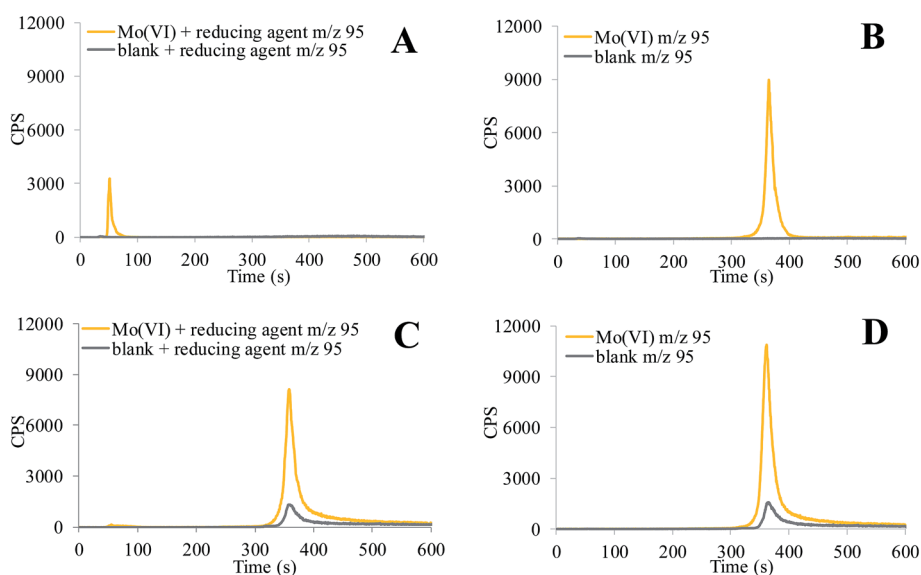

Fig. 3   Separation of (A) Mo(VI) solution (pH 5) in the presence of a reducing agent 0.0002 g L^{-1} Na$_2$SO$_3$, (B) Mo(VI) solution (pH 5), (C) Mo(VI) solution in 0.2% NaOH + 0.3% Na$_2$CO$_3$ buffer (pH 12) in the presence of a reducing agent 0.0004 g mL^{-1} Na$_2$SO$_3$ and (D) Mo(VI) solution in 0.2% NaOH + 0.3% Na$_2$CO$_3$ buffer (pH 12) applying the HPLC-ICP-MS procedure (20 ng mL^{-1} of Mo).

2204 | J. Anal. At. Spectrom., 2017, 32, 2200–2209
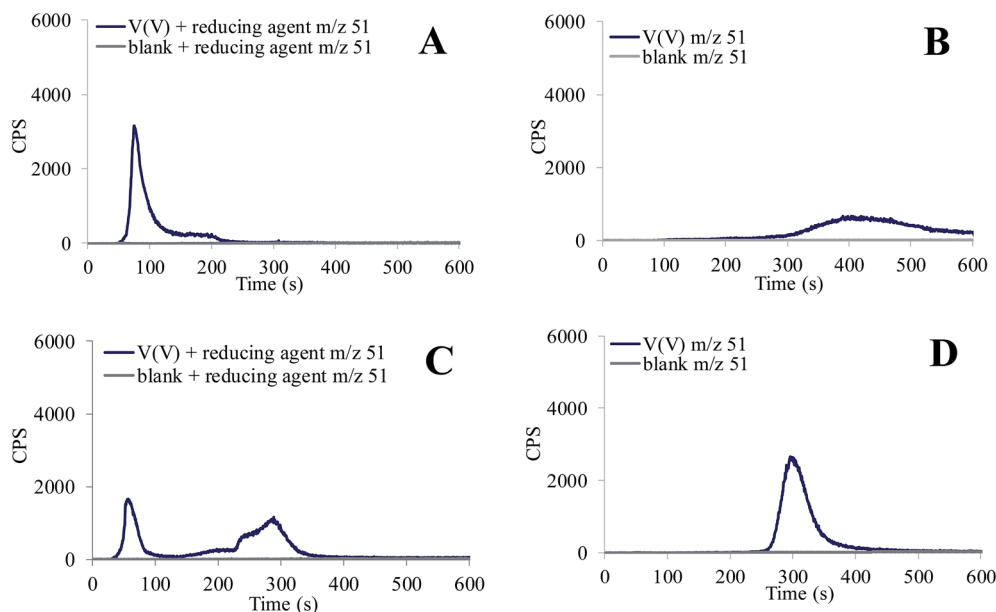
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Fig. 4 Separation of (A) V(v) solution (pH 5) in the presence of a reducing agent 0.0002 g L^{-1} Na$_2$SO$_3$, (B) V(v) solution (pH 5), (C) V(v) solution in 0.2% NaOH + 0.3% Na$_2$CO$_3$ buffer (pH 12) in the presence of a reducing agent 0.0002 g mL^{-1} Na$_2$SO$_3$ and (D) V(v) solution in 0.2% NaOH + 0.3% Na$_2$CO$_3$ buffer (pH 12) applying the HPLC-ICP-MS procedure (20 ng mL^{-1} of V).

of the V(v) chromatographic signal, while V species in the lower oxidation states are eluted with the solvent front (Fig. 4C).

From the data in Fig. 1–4 it can be concluded that under the chromatographic conditions applied, speciation of chromate, arsenate, molybdate and vanadate is possible at highly alkaline pHs.

3.2. Simultaneous speciation of chromium, arsenic, molybdenum and vanadium species by the HPLC-ICP-MS method

To demonstrate the capability of the HPLC-ICP-MS analytical procedure for simultaneous speciation analysis, a multiple working standard solution containing 20 ng mL^{-1} of chromate, arsenate, molybdate and vanadate was prepared in alkaline buffer (pH 12). Separated elemental species of Cr, As, Mo and V were simultaneously detected by ICP-MS recording m/z 52, 75, 95 and 51, respectively. A typical chromatogram is presented in
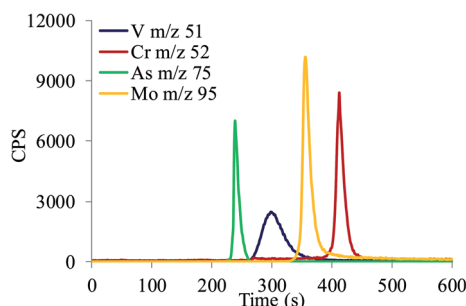

Fig. 5 Simultaneous separation of chromate, arsenate, molybdate and vanadate in 0.2% NaOH + 0.3% Na$_2$CO$_3$ buffer (pH 12) applying the HPLC-ICP-MS procedure (20 ng mL^{-1} of Cr, As, Mo and V).

Fig. 5. As evident, at pH 12, chromate, arsenate, molybdate and vanadate were eluted from 390 to 450 s, 230 to 270 s, 340 to 430 s and 270 to 380 s, respectively. Different elution times are related to different affinities of species for their retention on the anion-exchange resin. Since elution profiles were recorded at different m/z by ICP-MS, simultaneous speciation analysis of chromate, arsenate, molybdate and vanadate can be performed in a single chromatographic run, although the molybdate peak partially overlapped vanadate and chromate peaks.

If samples contain significantly higher concentrations of vanadate compared to those of chromate, arsenate and molybdate, detection of V species is possible even at its low abundance (0.25%) ^{50}V isotope.[24] Since ^{50}V isotope shares the same mass with ^{50}Cr isotope (abundance 4.345%),[24] simultaneous speciation analysis of V at m/z 50 is possible only if V and Cr species are selectively separated to avoid isobaric interferences in ICP-MS measurements. An example of simultaneous separation of chromate and vanadate at m/z 50 in alkaline (pH 12) solution containing 100 ng mL^{-1} of Cr and 1000 ng mL^{-1} of V is presented in Fig. 6. As can be seen, chromate and vanadate are well separated and can be simultaneously recorded at m/z 50.

3.3. Figures of merit of the HPLC-ICP-MS analytical method used for simultaneous speciation of chromate, arsenate, molybdate and vanadate in alkaline samples

3.3.1. Column recoveries. Possible interactions between the column resin and chromate, arsenate, molybdate and vanadate were checked by calculating column recoveries. For this purpose, single standard solutions of chromate, arsenate, molybdate and vanadate (20 ng mL^{-1} as the element) were prepared in alkaline buffer (pH 12) and injected onto the column. Fractions eluted under the elution time typical for
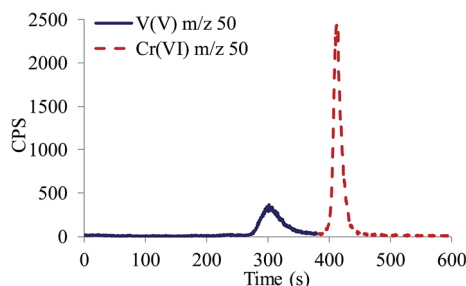
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J. Anal. At. Spectrom., 2017, 32, 2200–2209 | 2205

Fig. 6 Simultaneous separation of chromate and vanadate in 0.2% NaOH + 0.3% Na$_2$CO$_3$ buffer (pH 12) applying the HPLC-ICP-MS procedure (100 ng mL^{-1} of Cr and 1000 ng mL^{-1} of V). Chromatograms were recorded at m/z 50.

a particular species investigated were collected and the total elemental concentration was determined "off line" by ICP-MS. Column recoveries were calculated as the ratio between those concentrations of elemental species eluted and injected. The results are presented in Table 1.

As can be seen, for all the elemental species investigated column recoveries ranged between 99 and 105%, indicating that chromate, arsenate, molybdate and vanadate are quantitatively eluted and did not interact with the column resin.

3.3.2 Repeatability of measurements. The repeatability of measurements was tested for six consecutive simultaneous speciation analysis of a standard solution of chromate, arsenate, molybdate and vanadate, containing 20 ng mL^{-1} of Cr, As, Mo and V in alkaline buffer solution (pH 12). From results presented in Table 2 it is evident that the repeatability of measurements for the elemental species studied was found to be better than ± 3%.

Table 1 Column recoveries for separation of single elemental species of chromate, arsenate, molybdate and vanadate in 0.2% NaOH + 0.3% Na$_2$CO$_3$ buffer (pH 12) applying the HPLC-ICP-MS procedure. Results represent the mean value of three replicate determinations of the selected element with the standard deviation of the measurements

Species	Concentration of element added (ng mL^{-1})	Concentration of element found (ng mL^{-1})	Recovery (%)
Cr(VI) m/z 52	20.0 ± 0.2	19.8 ± 0.2	99
As(V) m/z 75	20.0 ± 0.2	19.8 ± 0.2	99
Mo(VI) m/z 95	20.0 ± 0.2	21.0 ± 0.2	105
V(V) m/z 51	20.0 ± 0.2	20.0 ± 0.2	100

3.3.3. Limits of detection. Limits of detection (LODs) and limits of quantification (LOQs) for the determination of chromate, molybdate, arsenate and vanadate by HPLC-ICP-MS were calculated as the concentration that provides a signal (peak area) equal to 3s and 10s, respectively, of the blank sample in the chromatogram. To calculate LODs and LOQs, 8 blank samples of the alkaline buffer solution (0.2% NaOH + 0.3% Na$_2$CO$_3$) were injected and Cr, As, Mo and V recorded at m/z 52, 75, 95 and 51, respectively. By the use of ICP-MS operating parameters summarized in Table S1,† the LODs and LOQs for chromate (m/z 52) were 0.2 and 0.67 ng Cr mL^{-1}, arsenate (m/z 75) 0.4 and 1.33 ng As mL^{-1}, molybdate (m/z 95) 1 and 3.33 ng Mo mL^{-1}, vanadate (m/z 51) 2 and 6.66 ng V mL^{-1} and vanadate (m/z 50) 100 and 333 ng V mL^{-1}, respectively. The method was proved to be of adequate sensitivity for the simultaneous speciation analysis of chromate, arsenate, molybdate and vanadate in leachates from building composites.

3.3.4. Linearity. The linearity of measurement for chromate (m/z 52), arsenate (m/z 75), molybdate (m/z 95) and vanadate (m/z 51) by the HPLC-ICP-MS was obtained over the concentration range from LOQ to 1500 ng mL^{-1}, while for vanadate recorded at m/z 50, from LOQ to 50 000 ng mL^{-1}. The correlation coefficients were better than 0.998 for all the elements investigated.

3.3.5. Accuracy check. As there is no certified reference material for the simultaneous determination of chromate, arsenate, molybdate and vanadate available, the accuracy of the analytical procedure was checked by the spike recovery test. For this purpose, multiple standard solution of chromate, arsenate, molybdate and vanadate (pH 12), containing 50 ng mL^{-1} of Cr, 100 ng mL^{-1} of As, 50 ng mL^{-1} of Mo and 500 ng mL^{-1} of V was added to the leachate sample, composed of 99.5% mixture (70% fly ash + 30% cement) and 0.5% EAF dust, one day after immersion into MilliQ water. The sample was diluted 1 : 2 with alkaline buffer before analysis. The recoveries were calculated as a ratio between found and added element concentration. The results are presented in Table S2.†

Data from Table S2† indicate that recoveries for chromate, arsenate, molybdate and vanadate of the spiked leachate sample lay between 98 and 102%, which confirmed the accuracy of the analytical procedure.

3.4. Simultaneous speciation analysis of chromate, arsenate, molybdate and vanadate in leachates from building composites by HPLC-ICP-MS at different concentration levels of vanadate

The analytical procedure developed for the simultaneous speciation analysis of chromate, arsenate, molybdate and

Table 2 Repeatability of measurement tested for six consecutive speciation analysis of a standard solution of chromate, arsenate, molybdate and vanadate, containing 20 ng mL^{-1} of Cr, As, Mo and V

| Species | Peak area | | | | | | Average | RSD% |
	1	2	3	4	5	6		
Cr(VI) m/z 52	103 518	110 234	110 873	104 262	107 832	105 342	107 010	2.9
As(V) m/z 75	13 138	12 959	13 359	13 483	13 101	13 408	13 241	1.6
Mo(VI) m/z 95	133 624	134 412	134 320	136 870	134 482	131 434	134 190	1.3
V(V) m/z 51	84 034	82 286	84 585	82 317	81 145	85 777	83 357	2.1

2206 | *J. Anal. At. Spectrom.*, 2017, **32**, 2200–2209

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vanadate was applied to the analysis of alkaline leachates from building composites. In this experiment, different building composites from fly ash, EAF dust and cement were prepared and immersed into MilliQ water for two different times (1 day or 9 months). Due to the presence of soluble $Ca(OH)_2$ and $CaCO_3$ arising from the building composites, the pH values of the leachates were highly alkaline.[20] In samples immersed for 1 day into MilliQ water the pH was 11, while in those immersed for 9 months, it was 13. To perform speciation analysis within the linear concentration range, leachate samples obtained 1 day after immersion into MilliQ water were diluted 1 : 2 with alkaline buffer. Sample aliquots were injected onto the column and the simultaneous speciation analysis performed following the procedure described in Section 2.5. In samples immersed into MilliQ water for 9 months, concentrations of vanadate were

significantly higher than those of chromate, arsenate and molybdate, so V detection was followed at m/z 50. The total concentrations of elements and elemental species in leachates are presented in Table 3, while their corresponding chromatograms in Fig. 7. As can be seen from the data of Table 3, sulphites and other reducing agents originating from building composites[20] triggered the reduction of chromate, arsenate, molybdate and vanadate. The Cr(vɪ), As(v), Mo(vɪ) and V(v) concentrations represented about 40–70% of their total elemental content. Data from Fig. 7 demonstrate that the HPLC-ICP-MS analytical procedure developed is applicable for the simultaneous speciation analysis of chromate, arsenate, molybdate and vanadate in highly alkaline leachate samples. Selective separation of chromate from vanadate and the possibility to detect the eluted V species by ICP-MS at the low

Table 3 Total concentrations of Cr, As, Mo and V determined by ICP-MS and concentrations of chromate, arsenate, molybdate and vanadate in leachates from building composites determined by HPLC-ICP-MS. (A1–A3) Leachates 1 day after immersion and (B1–B3) leachates 9 months after immersion into MilliQ water. Results represent the mean value of three replicate determinations of the selected element or elemental oxoanion species. The standard deviation of the measurements by ICP-MS is better than 1% and that of the HPLC-ICP-MS is better than 3%

| Sample/element	Concentration	Cr m/z 52 (ng mL^{-1})	As m/z 75 (ng mL^{-1})	Mo m/z 95 (ng mL^{-1})	V m/z 50 (ng mL^{-1})	V m/z 51 (ng mL^{-1})
A1	Total	65	220	130	—	1635
99.5% (70% fly ash + 30% cement) + 0.5% EAF dust	Oxoanion	47	173	80	—	1120
A2	Total	49	230	97	—	1570
99.5% (80% fly ash + 20% cement) + 0.5% EAF dust	Oxoanion	28	139	40	—	795
A3	Total	60	193	132	—	1477
100% (80% fly ash + 20% cement) + 0% EAF dust	Oxoanion	37	140	68	—	900
B1	Total	82	2030	820	—	9080
98% (80% fly ash + 20% cement) + 2% EAF dust	Oxoanion	42	1085	338	4445	—
B2	Total	85	2080	830	—	7110
98% (80% fly ash + 20% cement) + 2% EAF dust	Oxoanion	39	1130	325	4500	—
B3	Total	86	2090	840	—	9970
98% (80% fly ash + 20% cement) + 2% EAF dust	Oxoanion	44	1265	378	5290	—
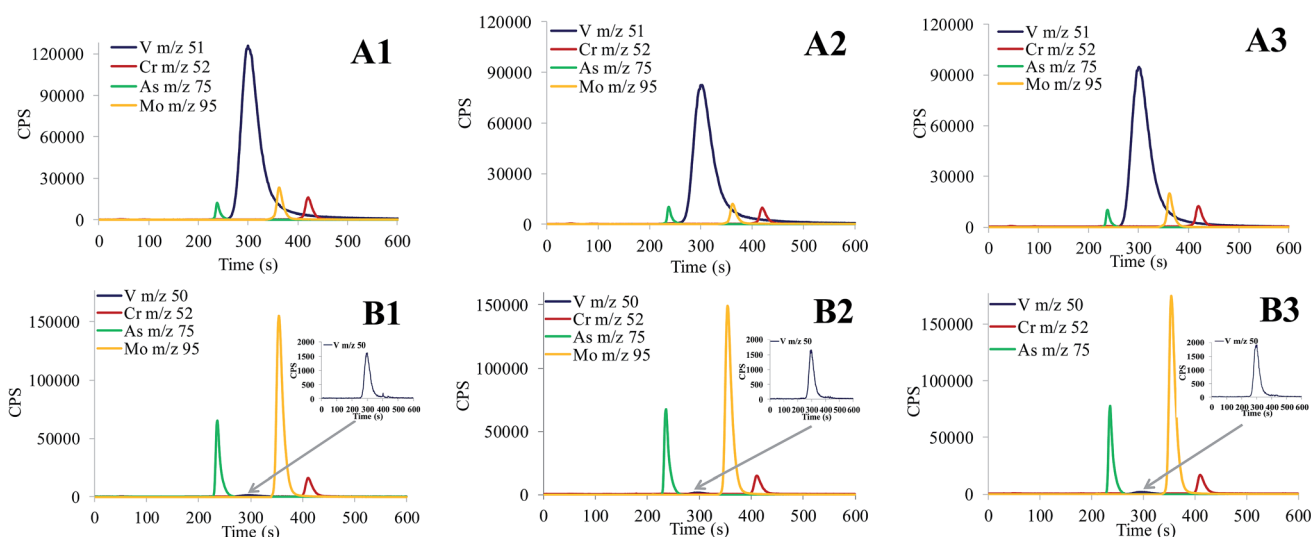
Fig. 7 Simultaneous separation of chromate, arsenate, molybdate and vanadate in leachates from building composites determined by HPLC-ICP-MS. (A1–A3) Leachate samples 1 day after immersion (samples diluted 1 : 2 with alkaline buffer) and (B1–B3) leachate samples 9 months after immersion into MilliQ water. Compositions of building composites are provided in Table 3.

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J. Anal. At. Spectrom., 2017, **32**, 2200–2209 | **2207**

abundance ^{50}V isotope extend its applicability for simultaneous speciation analysis to real world samples with significantly higher vanadate concentrations than chromate, arsenate and molybdate. The developed simultaneous speciation HPLC-ICP-MS procedure also appreciably reduces the time and the cost of analysis.

4. Conclusions

A novel analytical procedure for the simultaneous speciation analysis of chromate, arsenate, molybdate and vanadate by anion-exchange HPLC-ICP-MS is reported. In multiple standard solutions prepared at pH 12, the separated Cr, As, Mo and V species were quantitatively eluted from the column resin and detected on-line by ICP-MS, recording m/z 52, 75, 95 and 51, respectively. Under the chromatographic conditions applied, selective separation of Cr and V species was achieved. This enabled us to measure the eluted V species at the low abundance (0.25%) ^{50}V isotope, which is also the mass of ^{50}Cr isotope (abundance 4.345%). Using ^{50}V isotope in ICP-MS detection, simultaneous speciation analysis was possible in highly alkaline leachates of building composites containing significantly higher concentrations of vanadate than chromate, arsenate and molybdate. The developed analytical method is reliable, accurate (spike recoveries between 98 and 102%), repeatable (RSD < ±3.0%) and fast (chromatographic separation in 10 min). To the best of our knowledge, this is the first report on simultaneous HPLC-ICP-MS speciation analysis of chromate, arsenate, molybdate and vanadate in highly alkaline samples. The possibility of the use of ^{51}V and ^{50}V isotopes in ICP-MS detection extends the applicability of the method to simultaneous speciation analysis in samples with wide concentration ranges of vanadate.

Conflicts of interest

There are no conflicts to declare.

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J. Anal. At. Spectrom., 2017, **32**, 2200–2209 | **2209**