Short communication

Separation and detection of vanadate, tungstate, molybdate and chromate ions

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Abstract

Chromatographic separation and detection of four kinds of oxoanions were investigated. Ion-exchange chromatography and ion-pair chromatography with tetrabutylammonium hydroxide (TBA-OH) and with cetyltrimethylammonium bromide (CTMA-Br) as the ion interaction reagent (IIR) were compared. By using a carbon column, 1–3 mM solution of Na_3PO_4 as the eluent, and a permanent coating technique, these oxoanions could be separated satisfactorily without any influence of common anions. A solution of CTMA-Br in water–acetonitrile was allowed to flow through a carbon column (100×4.6 mm) until equilibration. Effective ion-exchange capacity can be controlled with the water–acetonitrile ratio of the solvent in which CTMA-Br is dissolved. The ion-exchange capacity of a column was 40 μequiv. when 2 mM CTMA-Br of 25% CH_3CN solution was used for the coating. Once coated, the column could be used for a long time without complement of the IIR. UV-absorbance detection showed fairly good sensitivity. If a multi-wavelength detector is used, ion identification is more reliable. The addition of H_2O_2 to the sample solution causes the vanadate peak to elute later. As an application example, Mo, V, W, and Cr in Hastelloy C-276 and ceramic pigments were determined after decomposition with Na_2O_2 in a zirconium crucible.   © 1997 Elsevier Science B.V.

Keywords: Ion-pair chromatography; Carbon column; Permanent coating; Inorganic cations; Metal oxoanions

1. Introduction

Metal ions are determined usually by spectrophotometric or spectroscopic methods, such as UV–Vis absorption, atomic absorption spectrometry (AAS), and inductively-coupled plasma atomic emission spectroscopy (ICP-AES). However, chromatographic methods offer several advantages; simultaneous multi-component and nondestructive determination, discrimination of the chemical state of the analyte, low degree of interference or influences by co-present components or matrices if the separation is achieved sufficiently. Chromatographic methods for some metal cations are popular today. On the

contrary, the separation of oxoanions of vanadium, tungsten, molybdenum, and chromium has been comparatively difficult using conventional ion-exchange methods. One reason is that these ions are likely to take various ionic forms in neutral or slightly alkaline medium. Another reason is the insufficient selectivity of the commercially-available stationary phase to these ions.

Zolotov et al. [1] reported the determination of tungstate, molybdate and chromate by suppression chromatography (IC) with a long separation column (500×3 mm) and sodium carbonate eluent (3.8 ml/min). Karmarker and Tabatabai [2] also separated tungstate and molybdate in a soil sample using suppression IC with carbonate eluents. With high pH eluents, it becomes possible to keep these oxoanions

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as their divalent monomer anions, but the selectivity for the separation is usually low. Some investigators [3–5] demonstrated that neutral or slightly alkaline medium was advantageous for the chromatographic separation of these oxoanions, because of the variability of the chemical characteristics of these oxoanions. However, hydrolysis and/or polymerization may give broad peaks. Mehra and Frankenberger determined trace amounts of molybdate [3] and tungstate [4] in soil samples using a single-column IC with an eluent containing hydroxybenzoic acid (pH 8.5). Because the conductivity detector is not selective, various kinds of anions are likely to influence the determination of these oxoanions. The use of a UV-absorbance detector could provide selectivity against unwanted ionic species. Goyal et al. [6] used a membrane suppressor for the reduction of the background absorbance due to carbonate ions to detect arsenate, selenate, etc., with a UV-absorbance detector. Marheni et al. [7] separated molybdate, chromate, and vanadate with an eluent containing NaCl and phosphate ions (pH 6.5) and a UV-absorbance detector. By using an ion-exchange technique with conventional columns, the separation of metal oxoanions is not so good. For this, the separation of anions using ion-pair chromatographic techniques [8,9] with reversed-phase columns and ion interaction reagents (IIRs) was thought to be advantageous, because of the higher resolution.

In the present investigation, a high pH and UV-transparent eluent, and an alkali-compatible column, are used to separate completely, and a UV detector is used to detect selectively, four kinds of oxoanions. The most successful combination was sodium phosphate eluent, a carbon column, with cetyltrimethylammonium bromide as the ion interaction reagent.

2. Experimental

2.1. Apparatus

The ion chromatographic system consisted of a pump (Hitachi L-6000), a loop injector (Rheodyne 7125, 100-μl loop), a UV-absorbance detector (Tosoh, UV-8000), and a custom-made data acquisition/processing system. Separation columns were a TSK-gel IC-anion PW (50$\times$4.6 mm) for ion-ex-

change chromatography and a TSK-gel Carbon 500 (100$\times$4.6 mm) for ion-pair chromatography.

2.2. Reagents

The eluents were aqueous solution of Na_3PO_4 and tetrabutylammonium hydroxide (TBA-OH) for the dynamic coating method [8], and Na_3PO_4 solution for the permanent coating method, in which cetyltrimethylammonium bromide (CTMA-Br) [9] in water–CH_3CN solvent was allowed to flow through the column for the coating of the IIR reagent onto the stationary phase. The apparent pH of 2 mM Na_3PO_4 was 10.8. Solutions of oxoanions were prepared by dissolving Na_3VO_4, Na_2WO_4, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, and K_2CrO_4. All regents were of analytical-reagent grade and used without further treatments. To obtain calibration lines for quantitative analysis, commercial standard solutions of each oxoanion (Wako) were used. Water was purified with a mixed-bed ion-exchange column and with a Milli-Q system (Millipore).

3. Results and discussion

3.1. Mobile and stationary phases

Sodium phosphate solution was chosen as the best eluent for the present purpose, because of its high pH, transparency in the UV region, the availability of the pure reagent, and the simplicity of preparation. The measured pH of the 2 mM solution was about 10.8. For the alkali-compatible stationary phase in ion-pair chromatography, a carbon column (100$\times$4.6 mm) was used both for dynamic-coating and permanent-coating techniques because of its chemical stability.

3.2. Separation with a conventional ion-exchange column

Fig. 1 shows the separation of four kinds of oxoanions, using an ion-exchange column widely used in non-suppressed IC. The retention times of vanadate and tungstate are very close, also that of molybdate and chromate. Poor separation is due to the insufficient resolution and selectivity of the
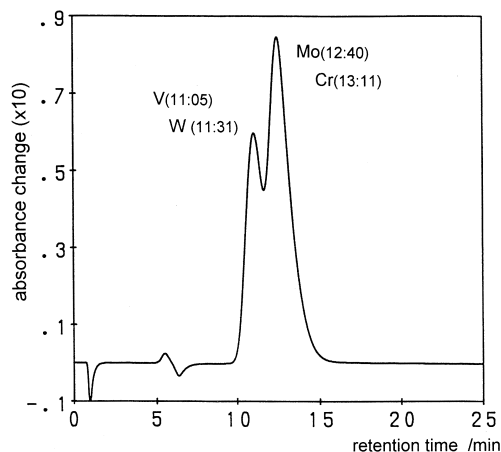
Fig. 1. Chromatogram of oxoanions with an anion-exchange column and phosphate eluent. Column: IC anion PW (50×4.6 mm); eluent, 1 mM Na$_3$PO$_4$ 1.0 ml/min; detection, UV 215 nm; sample, each ion 0.1 mM, 100 µl.
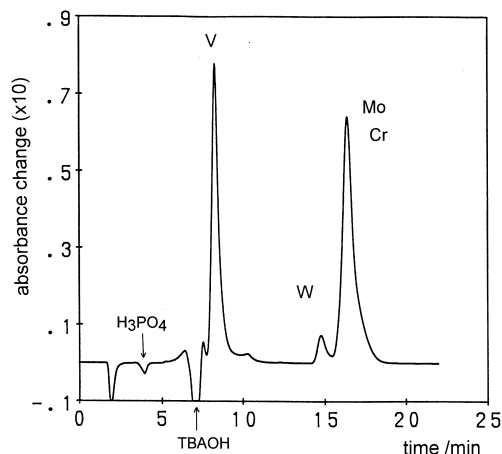

Fig. 2. Chromatogram of oxoanions with a carbon column and phosphate+tetrabutylammonium hydroxide eluent. Column, carbon 500 (100×4.6 mm); eluent, 1 mM Na$_3$PO$_4$+1 mM TBAOH 0.7 ml/min; detection, UV 220 nm; sample, each ion 0.05 mM, 100 µl.

stationary phase for these analytes. Modification of the eluent by the addition of some complex-forming reagents, such as tartrate or citrate, did not give any improvement. When H$_2$O$_2$ was added in 10 mM concentration, the vanadate peak shifted later but became very broad.

3.3. Separtion by ion-pair chromatography with tetrabutylammonium ion as the IIR

Dynamic-coating ion-pair chromatography give sharper peaks for the oxoanions as shown in Fig. 2. The theoretical plate number for vanadate was about 1300 and those for the others were about 4000. Molybdate and chromate peaks overlap severely. Moreover, two system peaks appear, one of which is close to and affects the vanadate peak. The separation was not improved by the concentration change of TBA-OH and sodium phosphate.

3.4. Separation by ion-pair chromatography with cetytrimethylammonium ion as the IIR

When the solution of CTMA-Br in water–acetonitrile was allowed to flow into a carbon column, CTMA ion was adsorbed strongly on the surface of the stationary phase. Because the CTMA ion is adsorbed very strongly, it is not necessary to add the

IIR reagent into the eluent. Once coated, IIR was not removed for at least 3 months of use, and can be cleaned-up with 100% CH$_3$CN. Fig. 3 shows a typical example of the separation of four kinds of oxoanions with 2 mM sodium phosphate as the eluent. The theoretical plate number for the vanadate peak was about 500, and those for the other peaks were about 2000. These numbers are a little smaller
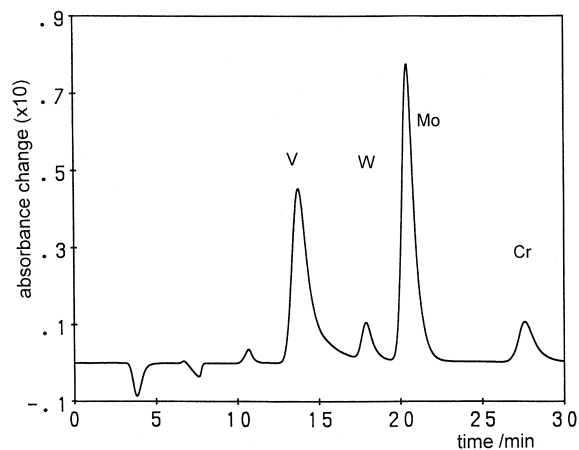

Fig. 3. Chromatogram of oxoanions with a carbon column+ cetyltrimethylammonium and phosphate eluent. Column, carbon 500 (100×4.6 mm)+CTMA; eluent, 2 mM Na$_3$PO$_4$ 0.5 ml/min; detection, UV 220 nm; sample, each ion 0.05 mM, 100 µl.
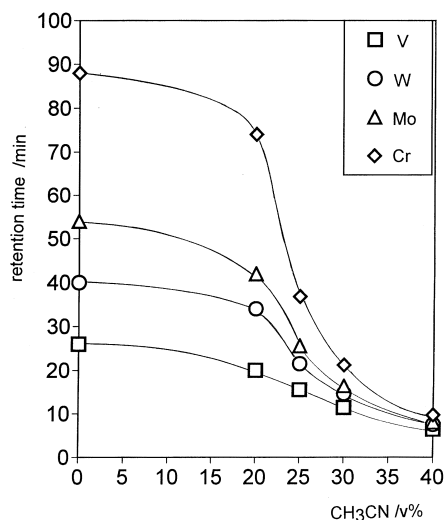
Fig. 4. Relation between the retention time of oxoanions and CH_3CN concentration in the coating solution. Column, carbon 500 (100×4.6 mm)+CTMA; eluent, 1 mM Na_3PO_4 0.7 ml/min.

than those given by dynamic-coating ion-pair chromatography. However, the separation of oxoanions is excellent. From the plot of the logarithm of the retention time vs. the logarithm of the phosphate concentration, it was indicated these ions are eluted as the divalent anions.

The effective ion-exchange capacity of a column depends on the amount of adsorbed IIR, and can be controlled by the acetonitrile concentration in which CTMA-Br is dissolved. Fig. 4 shows the relation between the concentration of acetonitrile and the retention times of the oxoanions. The ion-exchange capacity of a column was 40 μequiv. when 2 mM CTMA-Br of 25% CH_3CN solution was used for the coating. Once coated, the column could be used for a long time, for at least 3 months, without complement of the IIR.

UV-absorbance detection showed fairly good sensitivity. The detection limit is about 10^{-8} M for molybdate. Chromate can be detected more sensitively and selectively at 380 nm. If we use a multi-wavelength detector, ion identification is more reliable.

Table 1 shows the capacity factors of various UV active anions. The bromate and nitrate peaks are close to the vanadate peak. Apart from these ions, there may be no other ions interfering with the determination of oxoanions.

3.5. Effect of H_2O_2 on the retention of vanadate ions

When 1 ml of 35% H_2O_2 is added to a 1-l sample solution, only the vanadate peak shifts later, as shown in Table 1 (V-H_2O_2). It is indicated from the spectral change that the vanadate ion forms a complex with H_2O_2. Detection sensitivity of vanadium is enhanced about twice. Therefore, the addition of H_2O_2 in the sample solution is preferable in practical analysis. Wu and Schwedt [10] investigated on the HPLC of H_2O_2–oxine–bipyridine system for the separation of Cr, V and Mo. They used the formation of ternary peroxo complexes in acidic solution, with an H_2O_2 concentration larger than 1.5%. Our results indicate that vanadate forms specifically a stable and hydrophobic complex with H_2O_2 in alkaline medium.

3.6. Application to some solid samples

As practical examples of the application of the present method, three samples, Hasteroy (metal alloy), green and black pigments (ceramics) were analyzed. These samples could not be dissolved with acid. Fusion with Na_2O_2 was very effective and

Table 1
Capacity factor of various anions under the proposed elution condition

Ion	Capacity factor	Ion	Capacity factor	Ion	Capacity factor
IO_3^-	0.29	Br^-	2.17	V-H_2O_2	6.05
S.P.	0.59	HVO_4^{2-}	2.68	CrO_4^{2-}	6.84
NO_2^-	1.11	NO_3^-	3.47	I^-	17.22
CO_3^{2-}	1.73	WO_4^{2-}	3.95	SCN^-	56.9
BrO_3^-	1.74	MoO_4^{2-}	4.68		

Column, TSK gel carbon 500 (100×4.6 mm) coated with 2 mM CTMA-Br in 25% CH_3CN solution; eluent, 2 mM Na_3PO_4 0.5 ml/min.

Table 2
Analytical results of actual samples

	Hastelloy C-276 (%)		Green pigment		Black pigment	
	nominal[a]	found	nominal[b]	found	nominal[b]	found
W	3–4.5	3.53	—	—	—	—
V	0.35	0.27	1.21	0.95	—	—
Mo	15–17	13.34	—	—	0.95	0.74
Cr	14.5–16.5	14.21	20.60	19.92	37.95	37.25

[a]Indicated in a catalogue.
[b]values by ICP-AES.

convenient to ensure the dissolution state of V, W, Mo, and Cr as their divalent, monomer, oxoanions. Sample treatment scheme was as follows: (1) weigh 0.1 g of powdered or granulated sample into a zirconium crucible; (2) add 1.5 g of Na_2O_2, mix, heat for 10 min, and cool; (3) add 10 ml water and heat gently; (4) transfer the contents of the crucible into a 200-ml beaker, dilute with water and heat gently to decompose excess H_2O_2; (5) transfer the solution, if necessary filtrate through a filter paper, into a 500-ml volumetric flask and dilute to 500 ml (if the amount of precipitate is large, dissolution and re-precipitation are preferable); (6) dilute the above sample solution (filtrate) 10 times with water, if necessary, add little amounts of H_2O_2 (10 mM) at this stage and inject 100 μl into the chromatograph system.
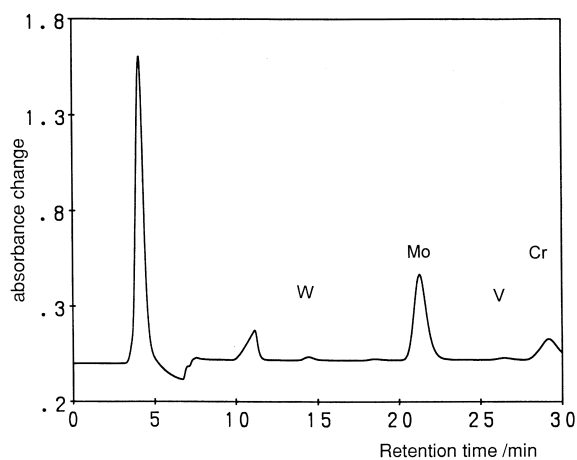
Fig. 5 is a chromatogram of the Hastelloy sample. The analytical results are summarized in Table 2. The determinations were successfully carried out. Because the detection limit is low (ca. 10^{-7} M for W, ca. 10^{-8} M for Mo), the sample amounts can be lowered to 1 mg if sample weighing is done precisely. The precision and accuracy of the present method depend on the dissolution and chromatographic determination processes. Careful treatment in the dissolution process may result in small errors, as in the usual chromatographic determinations. Detailed investigations on the precision and accuracy of the present method, in comparison with spectroscopic methods, are now in progress.

Fig. 5. Chromatogram of Hastelloy sample. Column, carbon 500 (100×4.6 mm)+CTMA; eluent, 2 mM Na_3PO_4 0.5 ml/min; detection, UV 220 nm.

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