A STUDY OF THE SEPARATION OF Mo(VI) AND W(VI) BY REVERSED PHASE HPLC

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The RP HPLC separation of Mo(VI) and W(VI) in the form of their oxoanions or anionic chelates with 2,3-dihydroxynaphthalene (DHN) was studied using a 100 × 4 mm i.d. column packed with Silasorb C18 (10 μm). The two elements were separated with a resolution of $R_{ij} = 1{\cdot}8$ in 10 min after injection of the DHN-derivatized anions into the stream (flow rate 1 ml min^{-1}) of the mobile phase containing phosphate buffer (50 mmol l^{-1}), DHN (0·5 mmol l^{-1}) and tetrabutylammonium cations (1 mmol l^{-1}) in 60% (v/v) methanol at pH 7.

Because of the close similarity of their chemical properties, Mo(VI) and W(VI) mutually interfere with their determination in solutions. In the present work, the possibility is examined of employing ion-pair interactions for the separation of the two elements in the form of their oxoanions or chelates with a polyphenolic reagent by reversed phase high performance liquid chromatography (RP HPLC). Previously, the interactions of onium cations with Mo(VI) and W(VI) oxoanions or their anionic chelates with polyphenolic ligands have been studied in aqueous solutions potentiometrically[1] and in two-phase extraction systems spectrophotometrically[2] and with the use of radionuclides[3,4].

EXPERIMENTAL

Chemicals and Solutions

Sodium molybdate and tungstate were recrystallized as described in ref.[5]. Their aqueous stock solutions at concentrations approximately 10 mmol l^{-1} were standardized gravimetrically with 8-hydroxyquinoline. Samples to be injected were prepared by dilution and contained 50% (v/v) methanol.

2,3-Dihydroxynaphthalene (DHN) (Loba Chemie, Austria) was recrystallized from ethanol and its purity was checked by HPLC (ref.[6]). Fresh solutions in methanol were prepared by weighing; injected solutions contained 50% (v/v) methanol.

The yellow solutions containing chelates of Mo(VI) and W(VI) with DHN were prepared by mixing aqueous solutions of the oxoanions with a methanolic solution of DHN; the concentration of Mo(VI) or W(VI) was between 1·5 and 25 μmol l^{-1}, that of DHN lay within the region

of 2 to 1 250 μmol l^{-1}. The methanol content was held at 50% (v/v). Acidity was adjusted with phosphoric acid to a value close to that of the mobile phase to which the samples were injected.

Tetrabutylammonium hydroxide (TBAH), 10% aqueous solution, pure (Lachema, Brno) was used as the ion pairing reagent. All the other chemicals used were of reagent grade purity (Lachema, Brno).

The mobile phase was prepared daily by mixing a methanolic solution of DHN with an aqueous solution of TBAH and H_3PO_4 and diluting with water to 1 000 ml. The resulting phosphate concentration was 50 mmol l^{-1}. Acidity of the aqueous solution was adjusted with NaOH and measured before mixing the solutions. This value is stated as the pH of the mobile phase.

Apparatus and Working Conditions

The chromatographic equipment consisted of a model 8500 syringe pump (Varian, U.S.A.), a PU 4021 multichannel UV/VIS detector (Pye Unicam, U.K.), and a TZ 4221 two-line recorder (Laboratorní přístroje, Prague). Stainless steel 100 × 4 mm i.d. column was slurry packed with 10 μm Silasorb C18, chemically modified silica gel (Lachema, Brno). Dead volume of the column was determined as the retention volume of thiourea. Samples were injected through a septum injector using Hamilton syringes.

Prior to use, the mobile phase was degassed in an ultrasonic bath. If the mobile phase composition was changed, the column was equilibrated by passing through it at least 200 ml of the new mixture. Measurements were performed at room temperature using a flow rate of 1 ml min^{-1}.

While solutions of DHN and the Mo(VI) and W(VI) oxoanions absorb in the UV region only, the yellow solutions of the chelates absorb also in the visible region, as far as about 400 nm. Based on a comparison of the absorption curves, wavelengths of 240 and 370 nm were chosen for the detection in the UV and visible regions, respectively. Absorption curves obtained during the passage of the bands through the detector cell were used for the identification of the solutes.

Acidity was measured with an OP-208 pH-meter equipped with an OP-0808-P glass–Ag/AgCl combined electrode and adjusted using phthalate and phosphate buffers (all Radelkis, Budapest).

RESULTS AND DISCUSSION

Chromatography of Mo(VI) *and* W(VI) *Using Mobile Phase Free of Chelating Agent*

When using a mobile phase only constituted by aqueous phosphate buffer at pH 7, the oxoanion samples injected were eluted in the dead volume. At higher acidities of the mobile phase the solutes were retained, considerable band tailing, however, took place. Leaving the peak shape unaltered, addition of methanol to the acid mobile phase only brought about a lowering in the capacity factors of the solutes.

In the presence of tetrabutylammonium counter-ions in the aqueous methanolic phase at pH 7, Mo(VI) injected in a concentration exceeding 5 mmol l^{-1} was eluted in the form of two symmetrical, well-resolved bands. On raising the mobile phase acidity to pH 4·9 and/or increasing the concentration of Mo(VI), the ratio of the peak height corresponding to the more retained band to the height of the peak at shorter rentention time increased. The same effect of the concentration of the oxoanion was

also observed for W(VI), but only at pH 4·9. The effect of concentration of the oxoanion injected into the mobile phase which contained tetrabutylammonium counter-ions is shown in Fig. 1. The absorption curves of the two bands measured during their passage through the detector cell after Mo(VI) or W(VI) injection were very similar. A feasible explanation of the occurence of two bands and the effect of sample concentration is in terms of separation of species with a different nuclearity, e.g. mononuclear (band with a lower retention) and oligonuclear species.

Injected into the mobile phase without DHN, the Mo(VI) and W(VI) chelates decomposed, and only the bands of free Mo(VI) or W(VI) and DHN were detected. The presence of tetrabutylammonium ions in the mobile phase had no effect on the stability of the chelates.

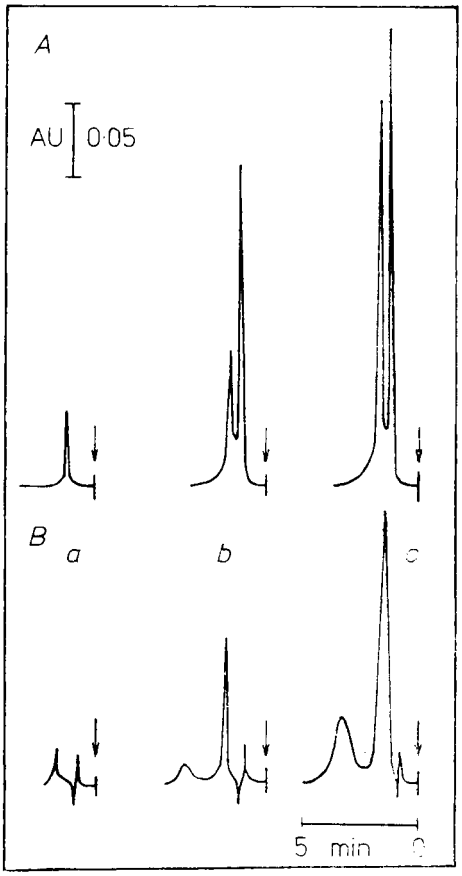

FIG. 1

Effect of concentration of Mo(VI) (*A*) or W(VI) (*B*) in sample on their ion pair chromatography in the absence of chelating agent. Volume injected 2 µl, *c*(Mo) or *c*(W) (mmol l^{-1}): *a* 5, *b* 10, *c* 100. Mobile phase: phosphate buffer (50 mmol l^{-1}), tetrabutylammonium ions (*A*: 5 mmol l^{-1}, *B*: 2 mmol . l^{-1}) in 70% (v/v) aqueous methanol, pH: *A* 7·0, *B* 4·9. Detection at 240 nm

Chromatography of Mo(VI) *and* W(VI) *Using Mobile Phase Containing* 2,3-*Dihydroxynaphthalene*

In the mobile phase at pH 3 containing DHN, the chelates decomposed; conditions favourable for their existence only established on lowering the mobile phase acidity to pH 5.

The effect of DHN concentration in the injected solution of Mo(VI) chelates on their chromotography is shown in Fig. 2. After the sample injection, a retained band of free DHN and a band of the Mo(VI) chelates eluted in the dead volume were detected. For the Mo(VI) chelates, the presence of free DHN was observed even at equimolar concentration of DHN and the oxoanion in the sample. The chelate peak heights were practically identical for samples containing Mo(VI) excess or DHN excess, respectively. In the former case, the free Mo(VI) chelated after the on-column injection, i.e., the chelation was relatively rapid and the insufficient amount of the chelating agent in the sample system was made up for by the DHN

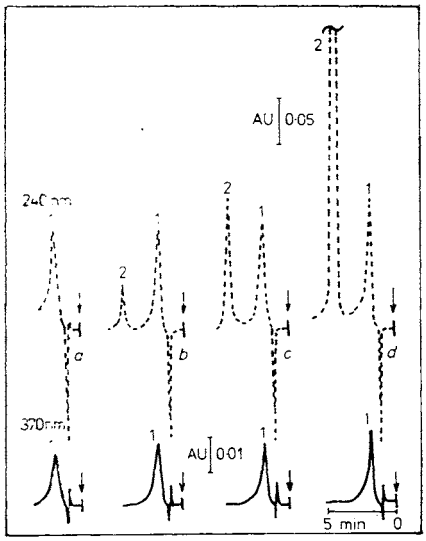

FIG. 2

Effect of concentration of DHN in sample on the chromatography of Mo(VI) chelates. Volume injected 5 µl, c(Mo) = 25 mmol l^{-1}, c(DHN)/c(Mo): *a* 0·5, *b* 1, *c* 5, *d* 50. Mobile phase: phosphate buffer (50 mmol l^{-1}), (0·5 mmol l^{-1}) in 45% (v/v) methanol, pH 5·0. Peaks: 1 chelate, 2 DHN

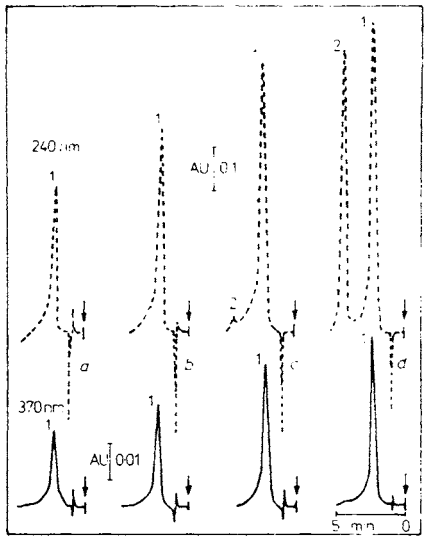

FIG. 3

Effect of concentration of DHN in sample on the chromatography of W(VI) chelates. Volume injected 5 µl, c(W) = 25 mmol l^{-1}, c(DHN)/c(W): *a* 0, *b* 0·5, *c* 1, *d* 10. Other conditions as in Fig. 2

present in the mobile phase. For tungsten, the chelate peak increased in height with increasing concentration of DHN in the sample (Fig. 3*b–d*), which can be explained by the slower chelation of the free W(VI) in the mobile phase as compared to Mo(VI). At absence of DHN in the sample, chelation of oxoanions was also observed after their injection into the stream of the weakly acid mobile phase containing DHN in a concentration of 0·5 mmol l^{-1} in 45 – 80% (v/v) methanol.

In the presence of tetrabutylammonium cations in the mobile phase, the chelates were retained. In accordance with the assumed behaviour of the anionic solutes, their capacity factors increased with increasing concentration of the tetrabutylammonium counter-ions; at a concentration of these ions of 10 mmol l^{-1} and a low methanol content of the mobile phase, 45% (v/v), the chelates did not elute even in several hours. Increase in the methanol content brought about lowering in the capacity factors for all the solutes.

Typical chromatograms obtained using the weakly acid mobile phase containing DHN and tetrabutylammonium ions are shown in Fig. 4. On the injection of the oxoanions, a negative peak whose height grew with the concentration of the oxoanions in the sample and that probably corresponded to the consumption of DHN from the mobile phase for the chelation, was observed at the retention time corresponding

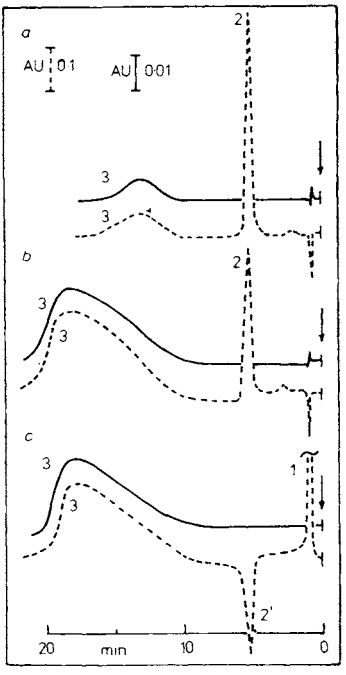

FIG. 4

Ion-pair chromatography of Mo(VI) chelates using mobile phase at pH 5. Volume injected 5 µl, c(Mo) = 25 mmol l^{-1}, c(DHN)/c(Mo): *a* 10, *b* 1, *c* 0. Mobile phase as in Fig. 2, c(TBA) = 1 mmol l^{-1}. Detection at 240 nm (dashed line) and 370 nm (full line). Peaks: 1 Mo(VI), 2 DHN, 2′ negative peak, 3 chelate

to DHN. We fail to offer an explanation of why this negative peak did not appear also in the absence of tetrabutylammonium ions in the mobile phase. If DHN was absent or present in a low concentration only, the peaks of the chelates were broad and nonsymmetrical. Increase in the concentration of DHN in the sample had a positive effect on the chelate peak shape and the capacity factors of the chelates decreased at the same time. These effects may be related with the chelating equilibria, because in weakly acid solutions and at higher concentrations of DHN, Mo : DHN (or W : DHN) 1 : 2 chelates are formed in addition to the 1 : 1 species. Moreover, at the acidity used, oligonuclear species can also be present in the samples at low DHN concentrations and relatively high concentrations of the oxoanions. The retention characteristics as well as the chelate peak shapes can be affected by changes in these equilibria brought about by interactions with the DHN present in the mobile phase and by the dilution of the sample injected.

When using a weakly acid aqueous-methanolic mobile phase containing DHN, and also tetrabutylammonium ions, the Mo(VI) and W(VI) chelates remained unseparated. Changes in the methanol content and tetrabutylammonium ion con-

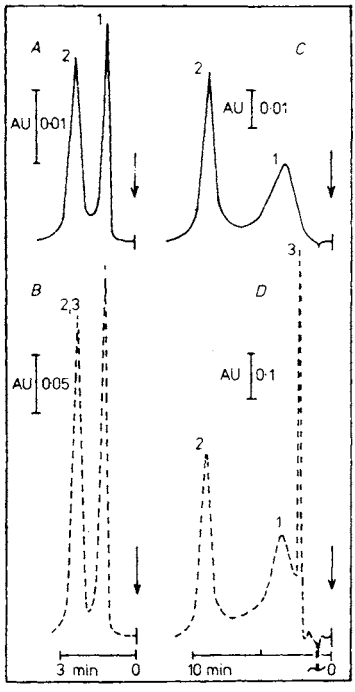

FIG. 5

Chromatography of Mo(VI) and W(VI) chelates using mobile phase at pH 7. Volume injected 5 µl, $c(\mathrm{Mo}) = c(\mathrm{W}) = 6$ mmol l^{-1}, $c(\mathrm{DHN})/c(\mathrm{Mo}) = 5$. Mobile phase: phosphate buffer (50 mmol l^{-1}), DHN (0·5 mmol . l^{-1}), tetrabutylammonium ions (in *C* and *D* only: 1 mmol l^{-1}) in 60% (v/v) methanol, pH 7·0. Detection at 240 nm (dashed line) and 370 nm (full line). Peaks: 1 Mo(VI) chelate, 2 W(VI) chelate, 3 DHN

centration affected the retention characteristics of the chelates equally for Mo(VI) and W(VI), their retention ratio remained unaltered.

Decrease in the mobile phase acidity to pH 7 gave rise to differences in the retention of the chelates of Mo(VI) and W(VI), respectively. In the absence of the tetrabutylammonium counter-ions from the mobile phase containing 60% (v/v) methanol, the chelates were separated with a resolution of $R_{ij} = 1{\cdot}4$ (Fig. 5*A*, *B*). Chelates of W(VI) were eluted together with DHN. After injection of an oxoanion mixture, a band of Mo(VI) chelates was eluted whereas W(VI) remained unchelated. If tetrabutylammonium counter-ions were added to the mobile phase at pH 7, the capacity factors of the chelates increased whereas that of DHN were affected negligibly. Bands of chelates of Mo(VI) and W(VI) as well as of chelates of Mo(VI) and DHN were separated (Fig. 5*C*, *D*); for chelates of the two elements, the resolution was $R_{ij} = 1{\cdot}8$. The effects of the methanol content and concentration of the tetrabutylammonium ions on the retention of the chelates and DHN are summarized in Table I.

In the neutral medium at a sufficiently high concentration of DHN, virtually all Mo(VI) or W(VI) is bonded in the anionic chelate with the oxoanion-to-DHN ratio 1 : 2 (ref.[3]). The differences in the chromatographic behaviour of the chelates enable

TABLE I

Retention characteristics of DHN and Mo(VI) and W(VI) chelates; mobile phase: phosphate buffer (50 mmol l^{-1}) and DHN (0·5 mmol l^{-1}) in methanol–water mixture at pH 7·0. Tetrabutylammonium ions were absent from the mobile phase (A) or present in a concentration of 1 mmol l^{-1} (B)

$\varphi(CH_3OH)$ % (v/v)	Capacity factor k			Retention ratio r_{ij}		
	DHN	Mo_c	W_c	W_c/DHN	Mo_c/DHN	W_c/Mo_c
		A				
30	1·19	*a*	*a*	—	—	—
45	3·36	0·89	1·29	0·38	0·26	1·45
60	1·34	0·32	1·33	0·99	0·24	4·16
		B				
45	3·85	13·0	5·0	6·49	3·39	1·92
60	1·30	2·46	7·67	5·90	1·89	3·12
65	0·75	1·09	3·24	4·32	1·45	2·97
70	0·56	1·03	2·08	3·71	1·84	2·02
80	*b*	*b*	*b*	—	—	—

[a] Injected chelates decomposed; [b] solutes were unretained.

Mo(VI) and W(VI) to be separated from one another. At pH > 7 the separation would be hampered by decomposition of the chelates[3] and oxidation of DHN, eventually also by degradation of the silica gel-based stationary phase.

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