CHROMATOGRAPHY OF Mo(VI) AND W(VI) CHELATES WITH 2,3-DIHYDROXYNAPHTHALENE

Milan VRCHLABSKÝ, Naděžda POLLAKOVÁ and Aleš HRDLIČKA

Department of Analytical Chemistry, J. E. Purkyně University, 611 37 Brno

Received February 21, 1989
Accepted May 17, 1989

Mo(VI) and W(VI) were separated in the form of their anionic chelates with 2,3-dihydroxynaphthalene (DHN) by reversed phase ion-pair chromatography. The effect of the organic modifier content and concentration of tetrabutylammonium cations (TBA) in the mobile phase and the effect of concentration of DHN in the injected sample on the separation were studied. The best results were attained by using a mobile phase containing DHN (0·5 mmol dm^{-3}), TBA counter-ions (10 mmol dm^{-3}) and phosphate buffer (50 mmol dm^{-3}) in a medium of 30% (v/v) methanol and 30% (v/v) acetonitrile at pH 7 and by injecting Mo(VI) and W(VI) samples containing DHN in a tenfold excess. On a CGC glass column 150 × 3·3 mm i.d. packed with Separon SGX C18 (5 μm), the solutes were separated at resolutions of $R_{ij} = 1·0$ (DHN–Mo) and 1·6 (Mo–W). The detection limits at 240 nm were 0·5 and 0·2 nmol for Mo(VI) and W(VI), respectively.

Our previous paper[1] was devoted to the separation of oxo anions of Mo(VI) and W(VI) by reversed phase ion-pair high performance liquid chromatography. Successful separation was achieved only by chelating the oxo anions with 2,3-dihydroxynaphthalene (DHN) and using an aqueous-methanolic mobile phase at pH 7 containing tetrabutylammonium (TBA) counter-ions, DHN and phosphate buffer for elution.

Effects influencing the formation and stability of the chelates in the dynamic conditions of chromatographic separation are the object of the present work.

EXPERIMENTAL

Acetonitrile (Laborchemie Apolda, G.D.R.) was purified following ref.[2]. Mobile phase, prepared daily, contained DHN (0·5 mmol dm^{-3}), TBA cations (1—10 mmol dm^{-3}) and phosphate buffer (50 mmol dm^{-3}) in 40—80% (v/v) aqueous methanol or in a water–methanol–acetonitrile ternary mixture with the nonaqueous fraction 60 or 50% (v/v) at pH 7.

Two columns were used. Column A was stainless steel, 100 × 4 mm i.d., packed with the chemically modified silica gel Silasorb C18 (10 μm) (Lachema, Brno) applying the suspension technique. Column B was a CGC glass column 150 × 3·3 mm i.d. packed with Separon SGX C18 (5 μm) (all Tessek, Prague). Samples were injected on column A through a septum injector using Hamilton microsyringes, and on column B using a Rheodyne 7125 injector with a 10 μl

sample loop. The mobile phase flow rates were 1·0 and 0·5 ml min^{-1} for the column A and B respectively.

Detection was photometric at 240 nm, at which the oxo anions of Mo(VI) and W(VI) as well as DHN and the chelates absorb, and at 370 nm, where only the yellow chelates absorb.

The other chemicals and solutions, apparatus and measurement conditions were as in our previous work[1].

RESULTS AND DISCUSSION

Effect of Chelating Agent Concentration in Sample Injected

Results of previous study of the chelating equilibria[3,4] suggest that, in dependence on the concentrations of DHN and the Mo(VI) and W(VI) oxo anions, sample at pH 7 may contain the free oxo anions, free DHN and the oxo anion-DHN 1 : 1 and 1 : 2 chelates. The chelating equilibria will re-establish after sample injection into the mobile phase stream.

It has been found[1] that the mobile phase must contain DHN in a rather high concentration to prevent decomposition of the chelates injected. On the other hand, this concentration is limited because DHN absorbs strongly in UV-range during the photometric detection. A good compromise is a concentration of DHN in the mobile phase of 0·5 mmol dm^{-3}.

The effect of concentration of DHN in sample on the chromatography of the Mo(VI) chelates is shown in Fig. 1. The ratio of the 1 : 1 and 1 : 2 chelates in effluent vary in favour of the latter one as the concentration of DHN is increased. At $c(DHN)/c(Mo) = 3$, no 1 : 1 chelates are detected, and elution of a zone of free DHN is observed. The negative peak 2′ appearing in chromatograms of the samples with lower DHN concentration represents obviously a detector response involving in-

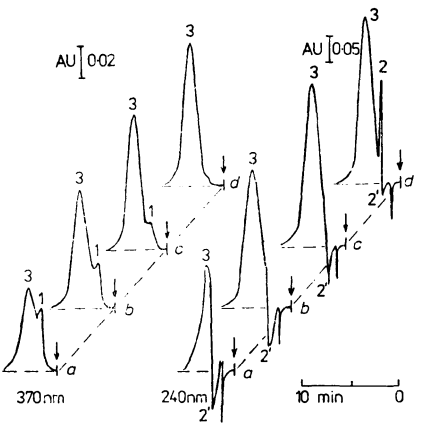

FIG. 1

Effect of concentration of DHN in sample on the chromatography of Mo(VI) chelates. Column A, mobile phase: DHN (0·5 mmol . . dm^{-3}), TBA hydroxide (5 mmol dm^{-3}), phosphate buffer (50 mmol dm^{-3}) in 60% (v/v) methanol at pH 7. Sample: $c(Mo) =$ = 3·8 mmol dm^{-3}, $c(DNH)/c(Mo)$: *a* 0, *b* 1, *c* 2, *d* 3; volume injected 10 µl. Peaks: 1 Mo-DHN 1 : 1 chelate, 2 DHN, 2′ negative peak, 3 Mo-DHN 1 : 2 chelate

crease of absorption by the zone of the 1 : 1 chelates and lowering of mobile phase absorption due to the consumption of DHN for chelation of free Mo(VI) and, if need be, for the bonding of another DHN ligand to the chelate. Elution of both the 1 : 1 and 1 : 2 chelate zones was also observed in the absence of the chelating agent in the sample.

Chromatograms of the samples of W(VI) oxo anions and chelates are shown in Fig. 2. Unlike samples containing Mo(VI), single chelate zone is eluted after injection of W(VI) samples. This zone is highly disperse if DHN is present in a low concentration or absent from the sample. The different behaviour of the two elements can be explained in terms of a substantially slower chelation kinetics in the case of W(VI). As the concentration of DHN in sample is increased, chelation of W(VI) is stimulated, and the chelate peak symmetry improves.

The Mo-DHN 1 : 2 and W-DHN chelate peak heights were measured in dependence on the concentration of DHN in sample injected. Present in sample in concentrations of $c(\mathrm{Mo}) = 3{\cdot}8$ or $7{\cdot}7$ mmol dm^{-3}, Mo(VI) elutes quantitatively in the form of its 1 : 2 chelate provided that DHN is present in the sample in an at least five-fold

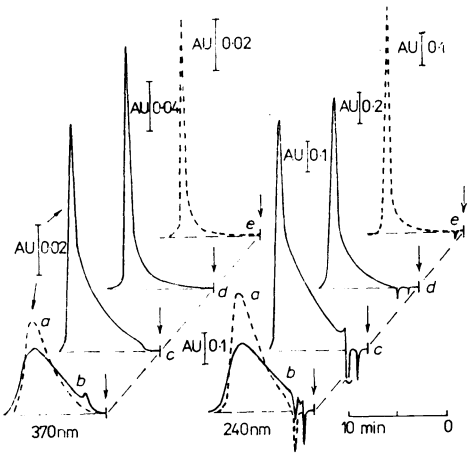

FIG. 2

Effect of concentration of DHN in sample on the chromatography of W(VI) chelates. Mobile phase as in Fig. 1 in 15% (v/v) methanol and 35% (v/v) acetonitrile (*a*, **e**) or in 60% (v/v) methanol (*b*—*d*). Sample: c(W) (mmol dm^{-3}), c(DHN)/c(W): *a* 3·8, 0; *b* 3·8, 0; **c** 3·8, 1; *d* 3·8 ,2; **e** 1·3, 2. Other conditions as in Fig. 1

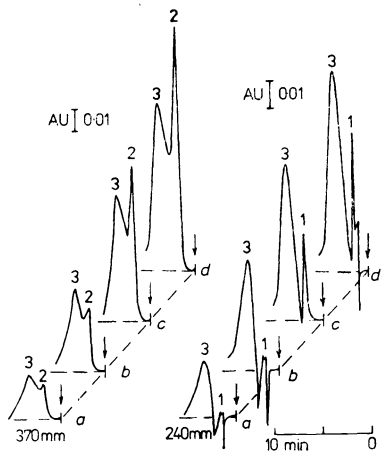

FIG. 3

Effect of concentration of Mo(VI) in sample on the chromatography of Mo(VI) chelates. c(Mo) (mmol dm^{-3}): *a* 1·8, *b* 3·0, *c* 7·5, *d* 11·3, other conditions as in Fig. 1. **Peaks: 1** Mo(VI), **2** Mo-DHN 1 : 1 chelate, **3** Mo-DHN 1 : 2 chelate

excess. At $c(W) = 3{\cdot}8$ mmol dm^{-3} in sample, the slope of the linear segment of the plot of W(VI) peak height vs DHN concentration is approximately five times higher than for Mo(VI). The height of the W(VI) chelate peak grows even at a six-fold excess of DHN in sample.

Chromatograms in Fig. 3 were obtained after the injection of Mo(VI) samples free from DHN. As the concentration of analyte is raised, the relative abundances of the 1 : 1 chelate and free Mo(VI) in effluent increase while that of the 1 : 2 chelate decreases. The sharp break between the peaks of Mo(VI) and its 1 : 2 chelate (peaks 1 and 3) observed in chromatograms registered at 240 nm arises from the lowering of mobile phase adsorption due to the consumption of DHN in the chelating equilibria and from the increase in absorption by the 1 : 1 chelate and the unchelated Mo(VI) zones.

Effect of Organic Modifier

Figure 4 shows the dependence of the capacity ratios of DHN and chelates of the two elements on the methanol content of the mobile phase. The retention of solute and, in particular, the capacity ratios of the chelates increase with decreasing concentration of methanol. At methanol concentrations of 60–70% (v/v) in the mobile phase (for given concentrations of the other components), the solute zones separate well in a relatively short time. When using the aqueous-methanolic mobile phase, W(VI) chelates give a highly asymmetrical peak; the symmetry improves if acetonitrile is added to the mobile phase.

The effect of acetonitrile was studied at total content of the nonaqueous solvents of 50 or 60% (v/v) (Fig. 5). The elution strength of the mobile phase increases and

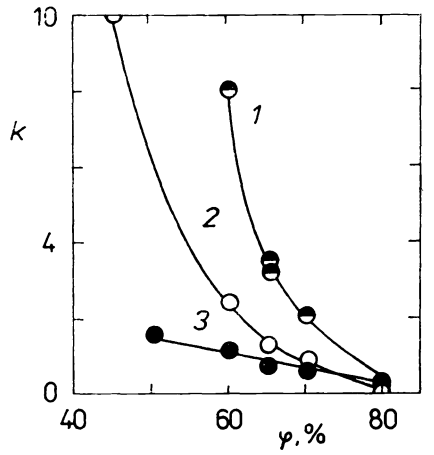

FIG. 4

Dependence of capacity ratios of chelates and DHN on the methanol content of mobile phase. Mobile phase as in Fig. 1 in 45–80% (v/v) aqueous methanol; sample: $c(Mo) = c(W) = 3{\cdot}8$ mmol dm^{-3}, $c(DHN) = 18{\cdot}8$ mmol dm^{-3}. Detection at 240 nm, other conditions as in Fig. 1. Curves: *1* W(VI) chelate, *2* Mo-DHN 1 : 2 chelate, *3* DHN

capacity ratios of all solutes decrease with increasing acetonitrile fraction. Addition of 30% (v/v) acetonitrile to a mobile phase containing 30% (v/v) methanol is sufficient for eliminating the peak asymmetry, and enables the time of analysis to be shortened without negative influence on the solute separation.

Effect of Concentration of Tetrabutylammonium Ions

The effect of concentration of TBA counter-ions on the separation of the chelates and DHN was examined in the aqueous-methanolic mobile phase as well as in the water–methanol–acetonitrile ternary phase (Fig. 6). Increase in the concentration of TBA ions brings about increased retention of the chelates while the retention of DHN is only negligibly affected. In the system free from acetonitrile, the resolution of the zones of the Mo(VI) chelates and DHN increases significantly; in the system with the ternary solvent system the separation of Mo(VI) chelates and W(VI) chelates

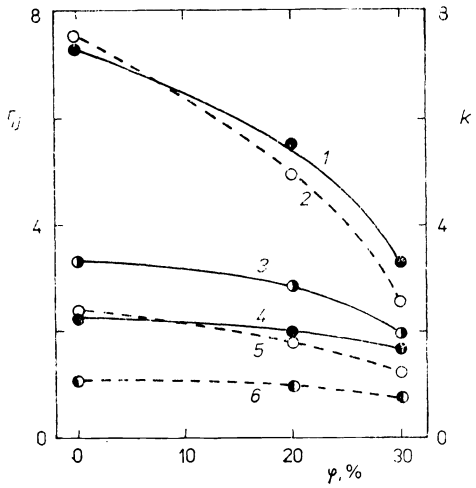

FIG. 5

Dependences of elution ratios and capacity ratios of solutes on the acetonitrile content in the water–methanol–acetonitrile mobile phase. Mobile phase containing 60% (v/v) nonaqueous solvents, other conditions as in Fig. 1, sample as in Fig. 4, detection at 240 nm. Full line: r_{ij}, curves: *1* W(VI) chelate/DHN, *3* W(VI) chelate/Mo(VI) chelate, *4* Mo(VI) chelate/DHN; broken line: *k*, curves: *2* W(VI) chelate, *5* Mo-DHN 1 : 2 chelate, *6* DHN

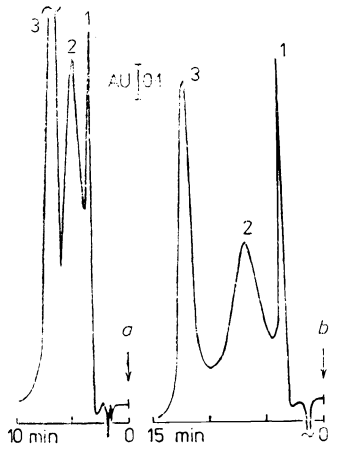

FIG. 6

Effect of concentration of TBA cations in water–methanol–acetonitrile mobile phase on the chromatography of chelates. Column B, mobile phase as in Fig. 1 in 30% (v/v) methanol, 30% (v/v) acetonitrile, c(TBA) (mmol dm^{-3}): *a* 5, *b* 10. Sample: c(Mo) = = c(W) = 1·9 mmol dm^{-3}, c(DHN)/ /c(Mo) = 10, volume 10 µl. Detection at 240 nm. Peaks: 1 DHN, 2 Mo-DHN 1 : 2 chelate, 3 W(VI) chelate

improves appreciably as well. However, if the concentration of TBA ions is raised to above 10 mmol dm^{-3}, the time of analysis extends substantially while no adequate effect on the separation ratios is achieved.

Application of Results

The chromatogram shown in Fig. 7 illustrates separation of Mo(VI) and W(VI) in the form of their anionic chelates with DHN on a glass column packed with silica gel with chemically bonded octadecyl groups (column B) using the water–methanol–acetonitrile ternary mobile phase of pH 7 containing DHN as the chelating agent, TBA counter-ions and phosphate buffer. Prior to injection, sample of Mo(VI) and W(VI) oxo anions was derivatized with excess of DHN.

Chelates of Mo(VI) and W(VI) respectively were separated in 14 min at a resolution $R_{ij} = 1{\cdot}6$. As compared to the results obtained previously[1], a better resolution of the DHN peak and the Mo(VI) chelate peak, $R_{ij} = 1{\cdot}0$, and improved separation efficiency for W(VI) chelates were achieved. The efficiency of separation of the Mo(VI) chelates remained relatively low, which may be due, e.g., to a more pronounced role of interactions of the Mo(VI) chelates with the residual silanol groups of the sorbent (substitution of the DHN ligand). The limits of detection calculated from the peak heights based on the signal/noise ratio equal to 2 were 0·5 nmol Mo(VI) and 0·2 nmol W(VI) measured at 240 nm wavelength.

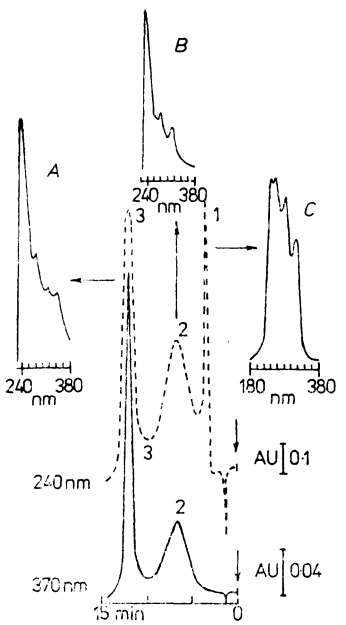

FIG. 7

Chromatography of Mo(VI) and W(VI) chelates with DHN and absorption curves of solutes. Mobile phase as in Fig. 6, c(TBA) = 10 mol dm^{-3}; sample as in Fig. 6, column B, detection at 240 nm (broken line) and 370 nm (full line). Absorption curves *A*, *B*, *C* measured at maxima of peaks 3, 2, 1, respectively. Peaks: 1 DHN, 2 Mo-DHN 1 : 2 chelate, 3 W(VI) chelate

REFERENCES

1. Vrchlabský M., Pollaková N., Hrdlička A.: Collect. Czech. Chem. Commun. *54*, 2133 (1989).
2. Riddick H. A., Bunger W. B. in: *Organic Solvents* (A. Weissberger, Ed.), p. 798. Wiley-Interscience, New York 1970.
3. Bartušek M.: Scr. Fac. Sci. Nat. Univ. Purk. Brun. *13*, 107 (1983).
4. Hrdlička A., Vrchlabský M.: Mikrochim. Acta (Wien) *1989*, II, 55.

Translated by P. Adámek.