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# Simultaneous determination of vanadium and molybdenum as N-benzoyl-N-phenylhydroxamate complexes by combining solvent extraction and liquid chromatography

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## Abstract

A normal-phase high-performance liquid chromatographic method for the selective simultaneous determination of vanadium and molybdenum with N-benzoyl-N-phenylhydroxylamine (BPHA) is described. The V(V)–BPHA and Mo(VI)–BPHA complexes were preconcentrated by solvent extraction into chloroform and injected on to a nitrile-bonded column for chromatography. The mobile phase was a  $5.9 \cdot 10^{-4}$  M solution of BPHA in chloroform (stabilized with amylene). The detection limits for vanadium and molybdenum were 2.1 and 3.3 ng ml<sup>-1</sup>, respectively, for an aqueous to organic phase-volume ratio of 20:1. The procedure, applied to the analysis of a synthetic water, showed satisfactory accuracy and precision.

*Keywords:* Complexation; Vanadium; Molybdenum; N-Benzoyl-N-phenylhydroxylamine; Metal ions

## 1. Introduction

There has been increasing attention to the analytical applications of LC for the separation and simultaneous determination of metal ions as their chelates with organic reagents [1–4]. A wide variety of organic reagents such as 4-(2-pyridylazo)resorcinol [5], 4-(2-thiazolylazo)resorcinol [6], dithizone [7], dithiocarbamates [8],  $\beta$ -diketones [9] and quinolin-8-ol [10] have been employed and metal ions have been determined by LC using on-column and precolumn derivatization methods.

Hydroxyamic acids constitute an important class of analytical reagents employed for the spectrophotometric and extraction–spectro-

photometric determination of species such as Fe(III), V(V), Mo(VI), Ti(IV), W(VI) and Zr(IV) [11]. Nevertheless, few data have been reported on the determination of metal ions by LC using these compounds. The best known reagent of this group is N-benzoyl-N-phenylhydroxylamine (BPHA) [12]. This reagent and most related hydroxamic acids form chelates that are insoluble in water but soluble in organic solvents such as chloroform. In those instances, it can be advantageous to use a liquid–liquid extraction step, followed by direct injection of the organic extract into a normal-phase system. This approach can provide a sensitive and selective method.

This paper reports the investigation of chromatographic conditions suitable for the separation of V(V) and Mo(VI) and their simultaneous

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determination at trace levels after precolumn chelation and extraction with BPHA into chloroform. The proposed method is almost free from interferences and has been applied to the analysis of a synthetic water with good results.

## 2. Experimental

### 2.1. Reagents and solutions

A vanadium stock standard solution ( $1000 \text{ mg l}^{-1}$ ) was prepared by dissolving 2.2966 g of ammonium metavanadate (Merck, Darmstadt, Germany) in 1000 ml of water. A molybdenum stock standard solution ( $1000 \text{ mg l}^{-1}$ ) was prepared by dissolving 1.8400 g of ammonium heptamolybdate tetrahydrate (Merck) in 1000 ml of water. Working standard solutions were prepared by appropriate dilution of the above solutions.

BPHA solutions were prepared by dissolving the appropriate amount of the reagent (Merck) in chloroform (stabilized with amylene). All solutions and solvents (liquid chromatographic grade) used to prepare the mobile phase were filtered through a  $0.45\text{-}\mu\text{m}$  membrane filter and degassed before use. Doubly distilled water was used for the preparation of all aqueous solutions. All the other reagents were of analytical-reagent grade.

### 2.2. Apparatus

A Hewlett-Packard (Avondale, PA, USA) Model 1050 liquid chromatograph, equipped with a variable-wavelength UV-visible detector, a Rheodyne (Cotati, CA, USA) Model 7125 loop injector with a  $20\text{-}\mu\text{l}$  sample loop and a Model 3396-A integrator, was used. A Spherisorb (Phase Separations, Deeside, UK) S5 nitrile column ( $250 \times 4.6 \text{ mm I.D.}$ ,  $5 \mu\text{m}$ ), linked to a Spherisorb guard column ( $10 \times 4.6 \text{ mm I.D.}$ ), was used for all separations.

UV-visible spectrophotometric measurements were performed with a Beckman (Fullerton, CA, USA) DU-8B high-performance spectrophotometer equipped with 1-cm silica cells.

### 2.3. Procedure

A sample containing less than  $7.5 \mu\text{g}$  of V(V) and  $20 \mu\text{g}$  of Mo(VI) was transferred into a 250-ml separating funnel and 20 ml of doubly distilled water and 36.4 ml of concentrated hydrochloric acid were added, the final volume being adjusted to 100 ml with distilled water. After shaking for 3 min with 5 ml of a 0.1% (w/v) solution of BPHA in chloroform, the organic phase was collected and dried over anhydrous sodium sulphate and filtered through a disposable syringe filter ( $0.2 \mu\text{m}$ ).

For LC analysis, the nitrile column was equilibrated at  $10^\circ\text{C}$  with chloroform (stabilized with amylene) containing  $5.9 \cdot 10^{-4} \text{ M}$  BPHA. A  $20\text{-}\mu\text{l}$  aliquot of the organic phase was injected, and the complexes were eluted at a flow-rate of  $0.6 \text{ min}^{-1}$ . The detection wavelength was 360 nm. Peak heights were measured for quantitative calculations.

## 3. Results and discussion

### 3.1. Spectrophotometric studies

V(V) and Mo(VI) can be extracted from an HCl medium at  $>3 \text{ M}$  with a BPHA solution in chloroform. We found that both ions were quantitatively extracted when  $4 \text{ M}$  HCl solution was shaken for 3 min with a 0.1% (w/v) BPHA solution in chloroform. Mo(VI) and V(V) complexes show absorbance maxima at 340 and 530 nm, respectively.

### 3.2. Chromatographic studies

Fig. 1 shows a typical chromatogram obtained from the injection of a chloroform extract of both complexes into a nitrile-bonded column, eluting with a solution of BPHA in chloroform. Although the absorption maxima are different, the complexes can be detected with good sensitivity at 360 nm.

An increase in the BPHA concentration in mobile phase leads to an increase in peak heights but a decrease in resolution, as can be seen in

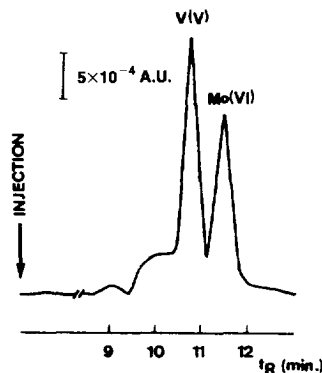


Fig. 1. Representative chromatogram of the complexes V(V)–BPHA and Mo(VI)–BPHA in a Spherisorb nitrile column ( $5 \mu\text{m}$ ,  $250 \times 4.6 \text{ mm}$  I.D.). Mobile phase,  $5.9 \cdot 10^{-4} \text{ M}$  BPHA in  $\text{CHCl}_3$ ; flow-rate,  $0.6 \text{ ml min}^{-1}$ ; column temperature,  $10^\circ\text{C}$ ; detection wavelength,  $360 \text{ nm}$ .

Fig. 2. The best chromatogram was obtained with  $5.9 \cdot 10^{-4} \text{ M}$  BPHA.

The graph of height equivalent to a theoretical plate ( $H$ ) versus flow-rate indicates that the maximum efficiency (minimum  $H$ ) is achieved with a flow-rate of  $0.6 \text{ ml min}^{-1}$ .

The effect of varying the column temperature

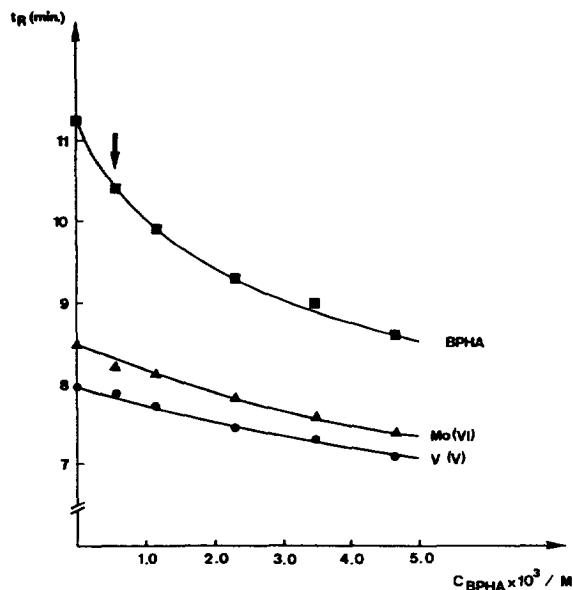


Fig. 2. Effect of BPHA concentration in the mobile phase on the retention times of the peaks. Flow-rate,  $0.8 \text{ ml min}^{-1}$ ; column temperature,  $20^\circ\text{C}$ ; detection wavelength,  $360 \text{ nm}$ .

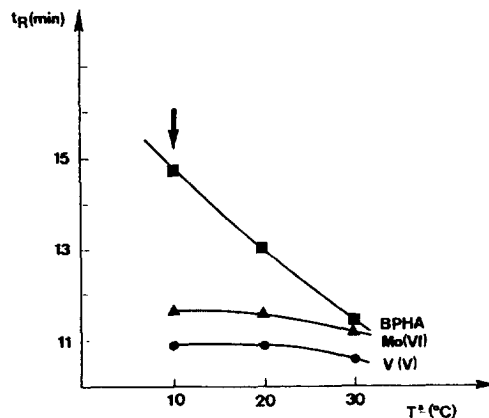


Fig. 3. Effect of column temperature on the retention times of the peaks. Mobile phase,  $5.9 \cdot 10^{-4} \text{ M}$  BPHA in  $\text{CHCl}_3$ ; flow-rate,  $0.6 \text{ ml min}^{-1}$ ; detection wavelength,  $360 \text{ nm}$ .

was evaluated by comparison of the chromatograms obtained at  $10$ ,  $20$  and  $30^\circ\text{C}$ . As shown in Fig. 3, the resolution of bands of molybdenum and vanadium complexes is unaffected, but the molybdenum and reagent bands tend to overlap as the temperature is increased. Further, the maximum peak heights were obtained when the temperature was kept at  $10^\circ\text{C}$ .

### 3.3. Calibration graph

The data were collected by well designed calibration experiments (using duplicate responses at each concentration and a randomized arrangement). Tests for non-linearity (for a univariate linear calibration) were based on the analysis of the residual variance from a regression into parts owing to “lack of fit” and “pure error”.

The calibration graphs were linear up to  $75 \mu\text{g l}^{-1}$  for vanadium and up to  $200 \mu\text{g l}^{-1}$  for molybdenum.

The repeatability of the method was  $5.38\%$  for V and  $3.14\%$  for Mo, expressed as the relative standard deviation (R.S.D.) for seven replicate analyses of solutions containing  $27$  and  $47 \mu\text{g l}^{-1}$ , respectively.

The detection limits for vanadium and molybdenum were evaluated according to the equation proposed by Snyder et al. [13] using a

signal-to-noise ratio of 2, and were 0.83 and 1.30 ng, respectively, which correspond to concentrations in the aqueous phase of 2.1 ng ml<sup>-1</sup> of vanadium and 3.3 ng ml<sup>-1</sup> of molybdenum, for an aqueous to organic phase-volume ratio of 20:1.

### 3.4. Interference studies

A detailed study of interferences was carried out for cations and anions in amounts ranging up to 8000 µg, with 8 µg of Mo and 4 µg of V. Ions were considered not to interfere if they produced an error in the peak height of less than 5%. The results obtained are summarized in Table 1.

The ions Hg(II) and I<sup>-</sup> can be completely removed, if necessary, before the procedure is applied, by evaporating the aqueous phase to dryness with nitric acid. The interference of Fe(III) can be eliminated by extraction into isobutyl methyl ketone from 6 M hydrochloric acid [14]. Bearing in mind that under these conditions Mo is partially co-extracted, it would be necessary to use two aliquots to determine both ions.

Table 1  
Effect of foreign elements

Ion	Tolerance ratio (w/w)	
	Ion/V(V)	Ion/Mo(VI)
Acetate, citrate, oxalate, ClO <sub>4</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup> , tartrate, F <sup>-</sup> , Br <sup>-</sup> , B <sub>4</sub> O <sub>7</sub> <sup>2-</sup> , As(V), Al(III), K(I), Li(I), Rb(I), Cs(I), Na(I), Cr(III), Mn(II), Ba(II), Cu(II), Ni(II), Sn(IV), Co(II), Cd(II), Pb(II), U(VI)	2000 <sup>a</sup>	1000 <sup>a</sup>
Ca(II), Zn(II), Sr(II), Mg(II), Bi(III), Se(IV), Ti(IV), As(III)	500	1000
Be(II)	100	1000
Tl(I)	250	750
Tl(II)	100	500
MnO <sub>4</sub> <sup>-</sup>	100	100
Hg(II), Fe(III)	25	1000
Zr(IV)	1000	100
W(VI)	2.5	100
I <sup>-</sup>	1	1000

<sup>a</sup> Maximum amount tested.

Table 2  
Composition of synthetic water sample

Ion <sup>a</sup>	Content (µg l <sup>-1</sup> )	Ion	Content (µg l <sup>-1</sup> )
As(V)	49.0	Pb(II)	23.7
Ba(II)	44.0	Mn(II)	28.0
Be(II)	19.0	<b>Mo(VI)</b>	<b>85.0</b>
Bi(III)	11.0	Ni(II)	49.0
Br <sup>-</sup>	94.0	Se(IV)	9.7
Cd(II)	20.0	Ag(I)	9.8
Cr(III)	18.6	Sr(II)	227.0
Co(II)	26.0	Tl(III)	8.0
Cu(II)	21.9	<b>V(V)</b>	<b>45.2</b>
Fe(III)	99.0	Zn(II)	66.0

<sup>a</sup> Added as nitrates, sulphates, chlorides or ammonium and sodium salts.

### 3.5. Determination of vanadium and molybdenum in a synthetic water

A synthetic water sample with the composition indicated in Table 2 was prepared and analysed by the proposed procedure using the standard additions method (SAM).

Table 3  
Results obtained in the determination of vanadium and molybdenum in a synthetic water sample

Parameter	V(V)			Mo(VI)		
	SAM <sub>1</sub>	SAM <sub>2</sub>	YC	SAM <sub>1</sub>	SAM <sub>2</sub>	YC
Slope	518 343	517 180	21 709	167 685	167 339	13 796
<i>n</i>	8	8	4	8	8	4
<i>s</i>	695.6	754.8	–	400.9	336.1	–
Youden blank [17]	There is no component error bias			There is no component error bias		
Comparison of slopes	No significant difference			No significant difference		
Comparison of results	No significant difference			No significant difference		
Content of analyte <sup>a</sup>	44.5 ± 7.1 μg l <sup>-1</sup> V			85.9 ± 10.5 μg l <sup>-1</sup> Mo		

Validation study was made using SAM with two test portions. SAM<sub>1</sub> = standard additions calibrations to a sample volume of 30 ml; SAM<sub>2</sub> = standard additions calibrations to a sample volume of 60 ml; YC = Youden calibration; *n* = number of measurements in a least-squares fitting set of data; *s* = standard deviation of the regression fitted line.

<sup>a</sup> Pooled content.

In order to obtain bias-free analytical results, by applying the SAM, it is necessary that the proportional interactive effect does not change with the matrix-to-analyte ratio [15,16]. This independence is evident from the observed linearity in the SAM plot [16], provided that the spike range is sufficiently large. An alternative

way of showing the lack of effect of the matrix-to-analyte ratio is to try another SAM plot at a different sample level.

We used the latter approach, applying the SAM at two sample volumes (Table 3, Fig. 4). Since the SAM slopes are the same in both cases (30 and 60 ml) for both vanadium and molybdenum, we have sufficient grounds [18] to accept the analytical results, 44.5 μg l<sup>-1</sup> of V and 85.9 μg l<sup>-1</sup> of Mo, as being free from interactive bias, because Tyson's requirement [15] is satisfied.

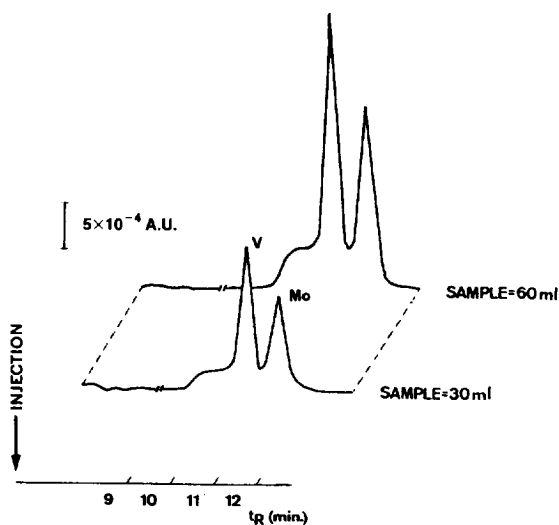


Fig. 4. Chromatogram showing the separation of vanadium and molybdenum in a synthetic water sample, with two different volumes of sample, using the proposed method.

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