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Journal of Alloys and Compounds 303–304 (2000) 132–136

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

A new spectrophotometric method for the determination and simultaneous determination of tungsten and molybdenum in polyoxometalates and their Ln(III) complexes

Stefan Lis*, Sławomir But

Department of Rare Earths, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

Abstract

A new spectrophotometric method is proposed for the determination of tungsten and molybdenum in polyoxometalates (POM) and their lanthanide(III) complexes (Ln/POM), using disodium-1,2-dihydroxybenzene-3,5-disulfate (Tiron), used as colorimetric reagent. Mo(VI) and W(VI) in solutions of polyoxotungstates and polyoxomolybdates can be determined from calibration graphs obtained by recording absorbancies in the wavelength range 352–500 nm for molybdenum and 352–400 nm for tungsten, where Beer's law is obeyed. This method can be also applied for the simultaneous determination of these elements in polyoxotungstomolybdates without previous chemical separation. The procedure is based on the recording of absorption spectra using values of absorbancies at two points on the spectrum. The content of Mo and W can be determined using an appropriate mathematical equation and molar absorptivity coefficients for each of two determined Mo and W ions at two points with the absorption spectrum. Calibration graphs for 2–10 (also to 40) μg/ml of Mo(VI) and 4–20 (also to 80) μg/ml of W(VI) were established by measuring the absorbance at 400 nm for molybdenum and at 352 nm for tungsten, respectively. Limiting concentrations of several interfering ions [P(V), V(V), Si(IV), As(III), Eu(III), Gd(III)] were evaluated. The standard error for measurements of all samples studied (POMs and their Ln(III) sandwiched and encrypted complexes) is <4%.

Keywords: Simultaneous determination of Mo(VI) and W(VI); Polyoxometalates; Spectrophotometry

1. Introduction

Polyoxometalates (POM) due to their wide applications in catalysis, oxidation chemistry, photochemistry, electron microscopy and as inorganic drugs have attracted much attention, particularly in recent years [1–4]. The majority of POMs have structures built of molybdenum and tungsten polyhedrons. Other elements present in these structures occur in small amounts. Polyoxotungstates and polyoxomolybdates decompose in alkaline media to form simple tungstate and molybdate ions, and in these forms they can be determined [5]. Tiron was used as a colorimetric reagent for molybdenum (VI) and was previously tested for variety of materials [6]. One of the classical problems in analysis is the simultaneous determination of two species in the same sample, without previous chemical separation. The method proposed here also enables the determination of Mo(VI) and W(VI) in the presence of other elements which occur in the structures of polyoxometalates and their complexes. The greater selectivity and a permissible large excess of several interfering ions make the new method superior to other described in literature, for example, to the spectrophotometric method with four preliminary extractions [7] or the technique based on precipitation with α-benzoinoxine [8].

2. Experimental

A Shimadzu UV-2401 PC spectrophotometer connected to an IBM Pentium 133 computer was used for all the measurements and treatment of data.

The pH of all solutions was adjusted to the value of 7.00±0.01 by addition of aliquots of NaOH or $HClO_4$, and was measured with of a microcomputer pH-meter CP-315 ELMETRON, equipped with the glass combination OSH-10-10 METRON electrode. All solvents and reagents used were of analytical grade. Tiron $C_6H_2(OH)_2(SO_3Na)_2 \times H_2O$ (FLUKA) was prepared daily as 8% solution and then diluted to the concentration of 1.6% in 25-ml calibrated flasks.

A buffer solution of pH~7.00 was prepared by mixing

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*Corresponding author.

0925-8388/00/$ – see front matter
PII: S0925-8388(00)00619-8

17.5 ml of 0.2 mol/l sodium hydroxide, NaOH, with 25 ml of 0.2 mol/l potassium acid phosphate, KH_2PO_4, and diluting to 100 ml with redistilled water. The standard molybdenum and tungsten solutions containing 1000 μg/ml were prepared by dissolving 1.8401 g of $(NH_4)_6Mo_7O_{24}\times 4H_2O$ and 1.7942 g of $Na_2WO_2\times 2H_2O$ in 1 l of redistilled water. The working solutions of mixtures of molybdenum and tungsten were prepared by mixing the solutions of these ions. The concentration of the standard solutions of interfering ions was 1000 μg/ml.

Solutions of polyoxometalates were prepared as described in [5]. To an aliquot of the POM (0.02–0.008 g) solution (ca. 100 mmol of molybdenum or/and tungsten), 2 ml of 1 mol/l solution of NaOH was added and the mixture was diluted with water to ~20 ml. The sample was then boiled gently for 2 h and evaporated to dryness. The dry solid residue was dissolved in 25 ml of redistilled water.

2.1. Procedure

Samples were prepared in 25-ml calibrated flasks. To an aliquot of ions to be determined, 5 ml of 8% solution of tiron and 5 ml of buffer solution were added and the pH was adjusted to 7.00±0.01. The absorption spectra in the range 300–750 nm (Fig. 1) were recorded with 1-cm quartz cells with water as the reference.

2.2. Theory

Consider a mixture of two compounds Mo(VI) (y) and W(VI) (x). If Beer's law is obeyed for both compounds over the whole wavelength range used and the path-length is l, the absorption spectrum of the mixture is defined by the equations:

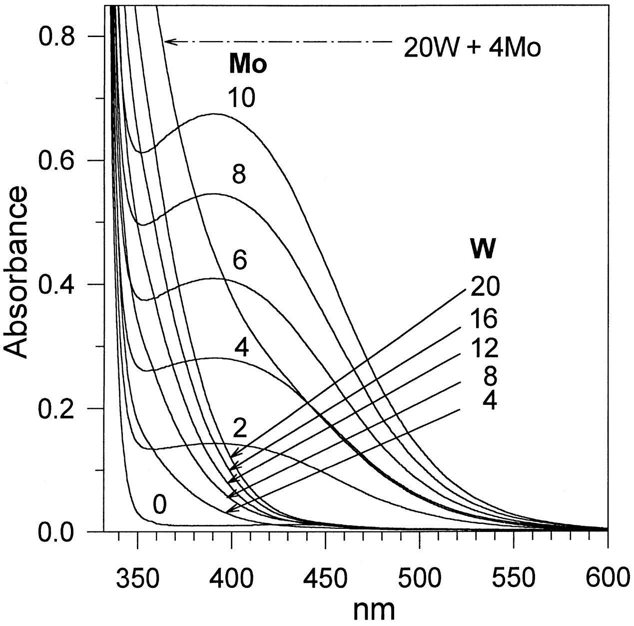

Fig. 1. Absorption spectra of the tungsten and molybdenum complexes with tiron (1.6%), in aqueous solution (pH=7.00±0.01), as a function of metal ion concentration.

$$A_{352} = (\varepsilon_x C_x + \varepsilon_y C_y) l \qquad (1)$$

$$A_{440} = (\varepsilon'_x C_x + \varepsilon'_y C_y) l \qquad (2)$$

where C_x, C_y are the concentrations of W(VI) and Mo(VI) ions, respectively; A_{352}, A_{440} the absorbances at 352 and 440 nm, respectively; ε_x, ε_y the molar absorptivities of W(VI) and Mo(VI), respectively, at 352 nm; ε'_x, ε'_y the molar absorptivities of W(VI) and Mo(VI), respectively, at 440 nm; and l the path-length.

The concentrations of W(VI) and Mo(VI) can be calculated from the following equations:

$$C'_{\mathrm{W(VI)}} = \frac{A_{352}\varepsilon'_y - A_{440}\varepsilon_y}{(\varepsilon_x \varepsilon'_y - \varepsilon'_x \varepsilon_y) l} \ [\mathrm{mol/l}] \qquad (3)$$

$$C_{\mathrm{W(VI)}} = \frac{C_{\mathrm{W(VI)'}}}{1000} \times 183.85 \times 10^6 \ [\mu\mathrm{g/ml}] \qquad (4)$$

$$C_{\mathrm{Mo(VI)}} = \frac{A_{440} - b(0)}{b(1)} \ [\mu\mathrm{g/ml}] \qquad (5)$$

$$C_{\mathrm{W(VI)}} = \frac{A_{352} - b(0)}{b(1)} \ [\mu\mathrm{g/ml}] \qquad (6)$$

where $b(0)$ and $b(1)$ are coefficients of calibration graphs, the intercepts and slopes, respectively.

Molybdenum (separately or in mixture with tungsten) can be determined by using the calibration graph at 440 nm, where, the absorption of tungsten is neglegible (Eq. (5)). Tungsten in mixture with molybdenum can be determined from the values of the absorbencies at 352 nm and 440 nm, using Eqs. (3 or 4). For the determination of tungsten (separately), a calibration graph at 352 nm is recommended (Eq. (6)).

3. Results and discussion

Fig. 1 shows the absorption spectra of the tungsten and molybdenum complexes with tiron in aqueous solution as a function of the Mo(VI) and W(VI) concentrations.

The calibration graphs obtained for different concentrations of molybdenum and tungsten, measured at appropriate wavelengths, are presented in Fig. 2. The molar absorptivities and the coefficients of the calibration graphs are presented in Table 1.

In all cases, the linear regression coefficients, r^2, were higher than 0.999, except for the calibration graph of tungsten at 440 nm ($r^2=0.922$).

Since the Pearson coefficient r^2 is not always a meaningful measure of the predictive power of a regression line, especially for small samples, the 95% confidence limits for four degrees of freedom are included in Fig. 2 graphs a–e.

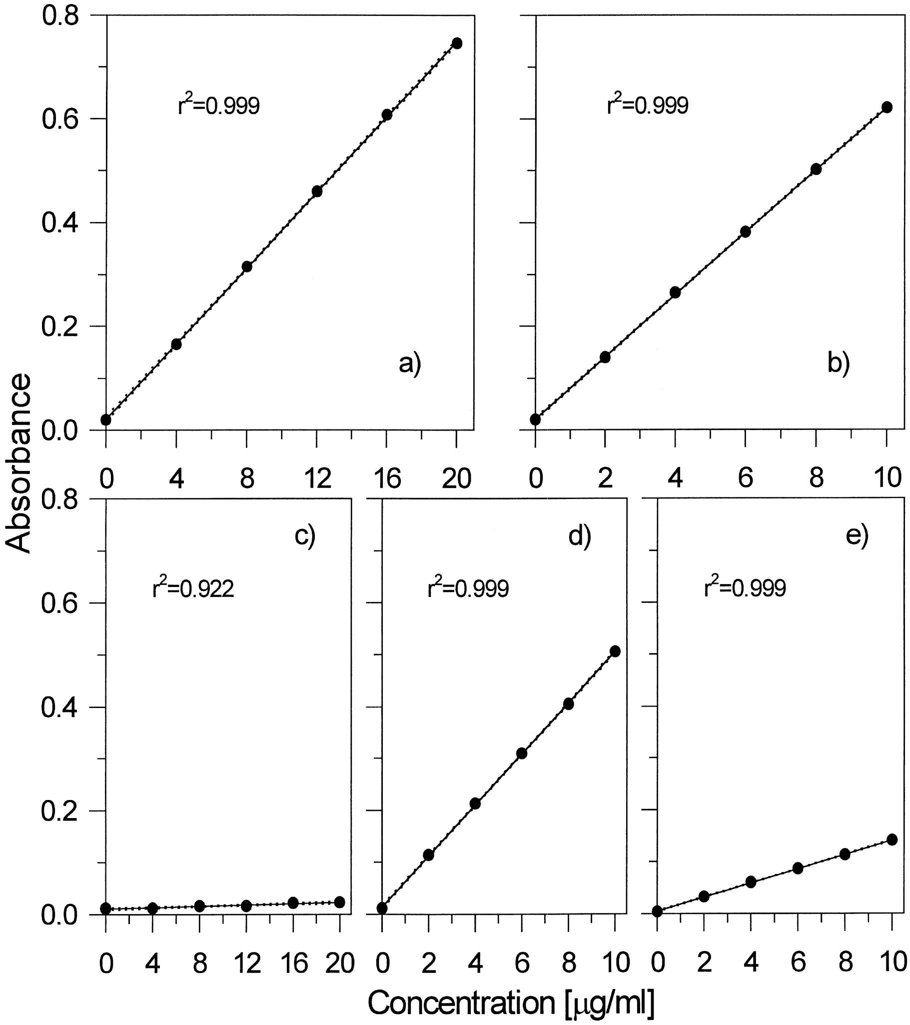

Fig. 2. Calibration graphs obtained for the determination of W(VI) at: 352 nm (a), 440 nm (c); and Mo(VI): 352 nm (b), 440 nm (d) and 500 nm (e), using the method proposed in this paper.

As is seen in the graphs a–e (Fig. 2) the regression line does not pass through $y=0$ at $x=0$. The point (0,0) is also outside the 95% confidence band. Hence, it is not appropriate to include (0,0) into the data set with high probability. Therefore, the detection limit on a 95% detection level has been assessed by blank measurements. The 95% detection limit is obtained from the intercept of the upper 95% confidence band with ordinate axes [9]. This data is included in Table 2, which summarizes the calibration parameters for the determination of W(VI) and Mo(VI).

The results concerning the determination of Mo(VI) and W(VI) binary mixtures of different compositions are summarized in Table 3. The determination of molybdenum in the presence of an excess of tungsten was also examined. In this case the calibration graphs at 460, 470 or 500 nm are proposed for the Mo(VI) determination, since tungsten does not interfere at these wavelengths.

The influence of several interfering ions, present in excess relative to Mo(VI) and W(VI), was also examined. The limiting concentrations of V(V), P(V), Si(IV), As(III),

Table 1
Molar absorption coefficients, ε, of Mo(VI) and W(VI) corresponding to the experimental wavelengths, λ_{exp}, of calibration graphs

	Tungsten		Molybdenum					
λ_{exp} [nm]	352	440	352	440	460	470	480	500
Symbol	ε_x	ε'_x	ε_y	ε'_y				
ε value	6701.3	115.8	5768.9	4710.7				
$b(0)$	0.02098	0.01022	0.02074	0.01386	0.01064	0.00830	0.00660	0.00489
$b(1)$	0.03645	0.00063	0.06013	0.04910	0.03545	0.02897	0.02283	0.01353

Table 2
Calibration parameters for W(VI) and Mo(VI) determination, corresponding detection limits (95%) and calculated concentration detection limits

Metal/wavelength	Slope ($\pm 1\ \sigma$)	Intercept ($\pm 1\ \sigma$)	d.l. ε [l/mol cm][a]	d.l. C [μg/l][a]
W 352 nm	$0.0364\pm0.0001_9$	$0.020\pm0.002_3$	0.027_3	0.17_3
Mo 352 nm	$0.0601\pm0.0002_4$	$0.021\pm0.001_5$	0.024_8	0.06_8
W 440 nm	$0.00063\pm0.0000_9$	$0.010\pm0.001_1$	0.013_3	4.90
Mo 440 nm	$0.0491\pm0.0002_5$	$0.014\pm0.001_5$	0.019_6	0.12
Mo 500 nm	$0.0135\pm0.0001_0$	$0.0049\pm0.0006_1$	0.006_5	0.12

[a] d.l., detection limit.

Table 3
Results of determination of Mo(VI) and W(VI) obtained for different binary mixtures

Composition of mixture [μg/ml]		Measured [μg/ml]		Standard error [%]	
Tungsten	Molybdenum	Tungsten	Molybdenum	Tungsten	Molybdenum
12.00	6.00	11.87	6.15	1.1	2.6
20.00	4.00	19.87	4.01	0.6	0.2
40.00	4.00	40.02	4.17	0.0	4.2
60.00	4.00	60.70	4.02[a]	1.2	0.6[a]
80.00	4.00	80.14	4.17[a]	0.2	4.2[a]
4.00	8.00	3.88	4.10	3.1	1.3
8.00	8.00	8.39	8.05	4.9	0.6
8.00	20.00	7.60	19.02	5.0	4.9

[a] $\lambda_{exp} = 500$ nm.

Table 4
Limiting concentrations of interfering ions in determination of Mo(VI) and W(VI)

Composition of mixture		Interfering ion added as	Limiting concentration of interfering ion [μg/ml]
4 [μg/ml] Mo	V	NH_4VO_3	0.08
4 [μg/ml] Mo	P	Na_3PO_4	80
4 [μg/ml] Mo	Sb	$SbCl_3$	10
4 [μg/ml] Mo	As	$NaAsO_2$	50
4 [μg/ml] Mo	Eu	$Eu(ClO_4)_3$	2.5
8 [μg/ml] W	Si	Na_2SiO_3	50
8 [μg/ml] W	As	$NaAsO_2$	100
8 [g/ml] W	P	Na_3PO_4	400

Sb(III), and Eu(III)] as interfering ions were evaluated and Table 4 shows the results obtained. In the case of V(V), a very strong interfering effect on the determination of Mo(VI) and W(VI) was observed. The method seems to be promising for the determination of vanadium and can be developed further for this purpose.

The proposed method was also satisfactorily applied to the determination of Mo(VI) and W(VI) in polyoxometalates and their lanthanide(III) complexes, and the results are summarized in Table 5. Although the limiting concentration of Eu(III), as an interfering ion, is rather low in comparison with concentrations of other elements studied

Table 5
Results obtained for determination of Mo(VI) and W(VI) in selected polyoxometalates and their lanthanide(III) complexes

Composition	Calculated [%]		Measured [%]		S.E. [%]	
$K_8SiW_{11}O_{39}\cdot 17H_2O$	62.8		64.7		3.0	
$K_7SiMo_2W_9O_{39}\cdot 17H_2O$	54.3	6.3	54.8	6.4	0.9	2.1
$K_7PMo_2W_9O_{39}\cdot 17H_2O$	55.0	6.4	54.4	6.6	1.1	2.5
$Na_9EuW_{10}O_{36}\cdot 19H_2O$	59.3		62.0		4.5	
$Na_9GdW_{10}O_{36}\cdot 19H_2O$	59.3		57.0		3.8	
$K_{10}P_2W_{17}O_{61}\cdot 27H_2O$	63.6		66.3		4.3	
$Na_6TeMo_6O_{24}\cdot 13H_2O$		35.5		35.6		0.2
$(NH_4)_2[Eu_2CeMo_{12}O_{42}]\cdot 29H_2O$		42.6		44.2		3.6
$K_{12}[(Eu)P_5W_{30}O_{110}]\cdot 20H_2O$	61.1		63.4		3.7	
$(Bu_4N)_{12}[(Eu)P_5W_{30}O_{110}]\cdot 10H_2O$	51.6		53.5		3.7	
$K_{12}[(Gd)P_5W_{30}O_{110}]\cdot 20H_2O$	61.1		63.0		3.1	
$Na_{27}[(Na)As_4W_{40}O_{140}]\cdot 71H_2O$	63.3		62.5		1.2	
$(NH_4)_{18}[(Na)Sb_9W_{21}O_{86}]\cdot 24H_2O$	54.3		56.0		3.1	

(Table 4), it does not interfere in the determination of Mo(VI) and W(VI). The value of 2.5 μg/ml is never exceeded in the determination of Eu(III) in Eu/POM complexes.

Salinas et al. [10] have proposed a spectrophotometric method, based on use of the first derivative of the ratios spectra, for the simultaneous determination of salicylic and salicyluric acids. We have tried to adapt Salinas's procedure to the determination of Mo(V) and W(VI), however, the results obtained were not satisfactory.

The method proposed in this paper permits the determination of Mo(VI) and W(VI) in the concentration range 2–10 μg/ml (also to 40 μg/ml) and W(VI) of 4–20 μg/ml (also to 80 μg/ml), respectively. The upper limits refer to the determination of Mo(VI) and W(VI) in POM structures (polyoxomolybdates or polyoxotungstates) not having both elements (Mo and W) present in the same sample. This method enables also the determination of Mo(VI) and W(VI) in the presence of other elements that occur in the structures of polyoxometalates and their complexes. In all cases the value of standard error is less than 4%.

Acknowledgements

This work was supported by the Polish State Committee for Scientific Research, Grant No. 3 T09A 106 14. The authors are grateful to Dr Günther Meinrath for his helpful discussion.

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