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NOTE

Extractive Separation and Direct Spectrophotometric Determination of Molybdenum with N-o-Tolyl-o-methoxybenzohydroxamic Acid

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Abstract

A new reagent, *N*-*o*-tolyl-*o*-methoxybenzohydroxamic acid (OTMBHA) is proposed for highly sensitive and selective determination of Mo(VI) by rapid extraction of its yellow complex with isoamyl alcohol and simultaneous spectrophotometric determination at 350 nm. The complex follows Beer's law at this wavelength over the concentration range 0.5 to 10.5 μg/ml, the sensitivity being 0.010 μg of Mo/cm^2 ($\varepsilon = 9.1 \times 10^3$). A 0.01 *M* reagent solution in isoamyl alcohol is adequate for complete extraction of molybdenum within 5 min. The method is found to be applicable to separation of molybdenum from many metals which constitute the nuclear fuels and fission products. Molybdenum was determined in steels.

INTRODUCTION

N-Phenylbenzohydroxamic acid and its analogs have been extensively utilized in liquid–liquid extraction and colorimetric determination of several metal ions (*1*) but studies on molybdenum are few. Benzohydroxamic acid (*2*) was used for simultaneous extraction of V(V) and Mo(VI) in hexenol. The method required subsequent reduction of Mo(VI) and interfering V(V), and determination of molybdenum as its thiocyanate complex. Several anions and cations interfered. Salicylhydroxamic acid was tried but it failed to ensure complete extraction of Mo(VI) (*3*). During studies on physicochemical properties and analytical applications of *N*-*o*-tolyl-*o*-methoxybenzohydroxamic acid (OTMBHA), it was observed that the reagent forms a yellow complex with Mo(VI) which is easily extractable in isoamyl alcohol. A method of extraction and determination of Mo(VI) as its complex with OTMBHA was then developed.

EXPERIMENTAL

All chemicals were reagent grade unless otherwise stated. Isoamyl alcohol was purified following the standard method (*4*). Molybdenum solution was prepared by dissolving ammonium molybdate in deionized water. Its molybdenum content was established volumetrically by the oxine method (*5*).

OTMBHA was freshly prepared following the general method of Gupta and Tandon (*6*). It was recrystallized repeatedly to a sharp, constant, melting point. It was then characterized by gas–liquid chromatography and IR and UV spectroscopy. The reagent is highly stable if stored in the dark. A stock solution (0.01 *M*) of the reagent was prepared in isoamyl alcohol.

pH measurements were carried out with a radiometer pH meter model PHM-29 (Hungary). The absorption spectra were recorded on a Perkin-Elmer 492–5000 spectrophotometer, and measurements at a constant wavelength were done with a SF-4 (USSR) spectrophotometer using matched quartz cells of 10 mm path length.

EXTRACTION PROCEDURE

To a 25-ml aliquot solution of Mo(VI) containing 0.5 to 10.5 μg of Mo/ml, 5 ml of 0.1 *M* potassium hydrogen phthalate solution was added and, with the help of 2 *N* HCl, its pH was adjusted between 1.5 and 2.5. The mixture was transferred to a 100-ml separatory funnel. About 10 ml of reagent solution was added and, after stoppering the funnel, the contents were shaken vigorously for 5 min. The aqueous and nonaqueous phases were allowed to separate, and the isoamyl alcohol extract was removed into a beaker containing anhydrous sodium sulfate. The aqueous layer was retained in the separatory funnel and extracted again with a fresh 10 ml portion of OTMBHA solution for 5 min. The extract, after phase separation, was removed and mixed with the first extract, transferred to a 25-ml volumetric flask, and made up to the mark with OTMBHA solution. The absorbance of the yellow extract was measured at 350 nm. A calibration curve was set by extraction determination of several known amounts of molybdenum and plotting the optical density values against the concentration of Mo(VI). The results were found reproducible within ±0.5%.

RESULTS AND DISCUSSION

Absorption Spectra

The absorption spectrum of the Mo-OTMBHA system in isoamyl alcohol against OTMBHA solution as blank is shown in Fig. 1. It shows a

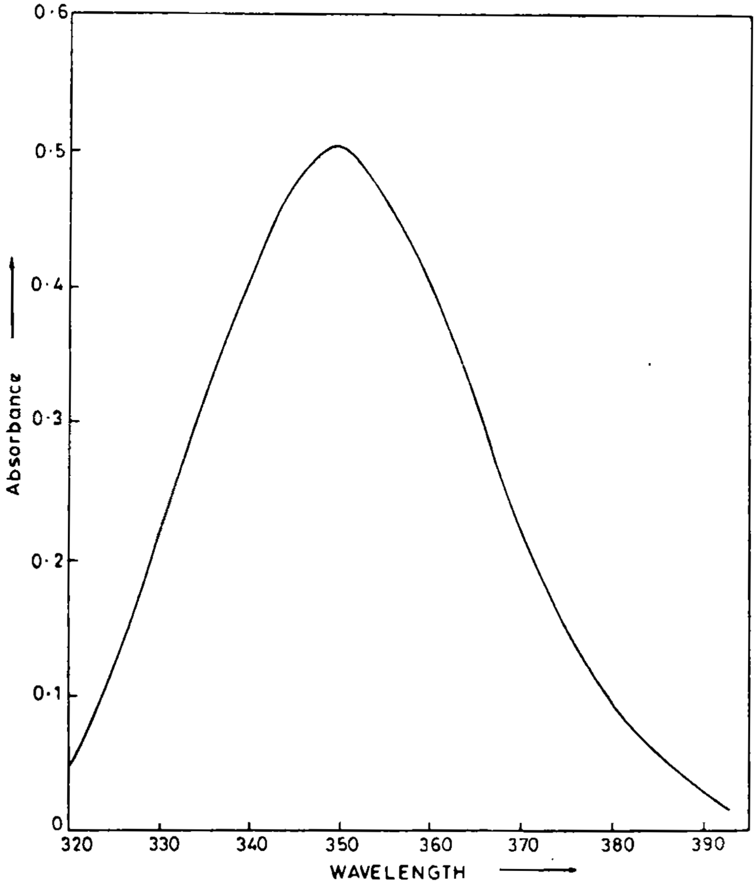

FIGURE 1.

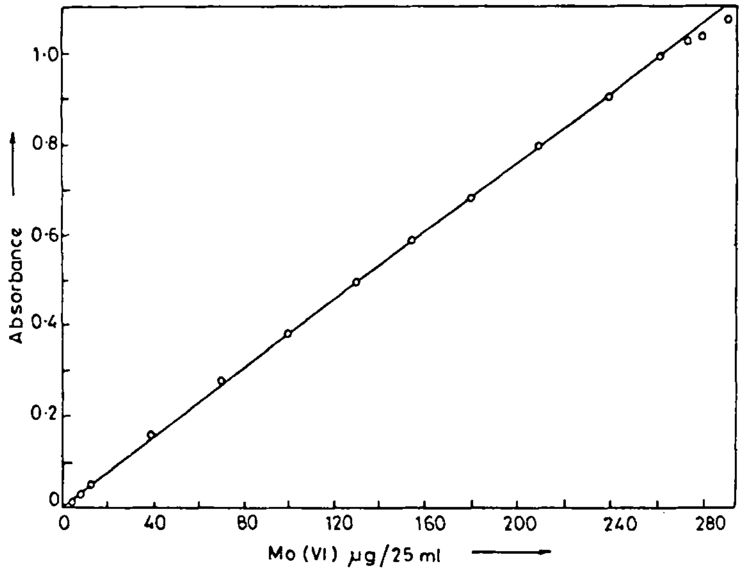

FIGURE 2.

peak at 350 nm, and all measurements were done at this wavelength. At this wavelength Beer's law is obeyed in the range 0.5 to 10.5 µg/ml (Fig. 2). The molar absorptivity is 9.1×10^3 $l/mole^{-1}$ cm^{-1}. The sensitivity of the present method, calculated according to the definition of Sandell (7), is 0.010 µg of Mo/cm^2. The color of the system is stable for several hours.

Effect of pH on Extraction

Twenty-five milliliter solutions containing 75 µg of Mo(VI) were adjusted to different pH values with the help of potassium hydrogen phthalate–hydrochloric acid buffers and extracted as described above. The results are presented in Table 1 (Fig. 3). It was found that the extraction is quantitative in the pH range 2 to 2.5, and nearly quantitative in the pH ranges 1 to 2 and 2.5 to 3.

Effect of Reagent Concentration

Extraction of 75 µg of Mo(VI) was carried out using 25 ml reagent solutions of 0.0002, 0.001, 0.01, and 0.05 *M* in OTMBHA, the time of equilibration being 5 × 2 min in each case. It was found that 0.01 *M* reagent solu-

TABLE 1

Extraction of Mo(VI)–OTMBHA Complex as a Function of pH

pH	Extraction E (%)	Distribution ratio, D
1 *N* HCl	80	4.0
0.1	85	5.7
0.5	90	9.0
1.0	96	24.0
1.5	98	49.0
2.0	100	∞
2.5	100	∞
3.0	96	24.0
3.5	86	7.3
4.0	80	4.0
5.0	75	3.0
6.0	65	1.9

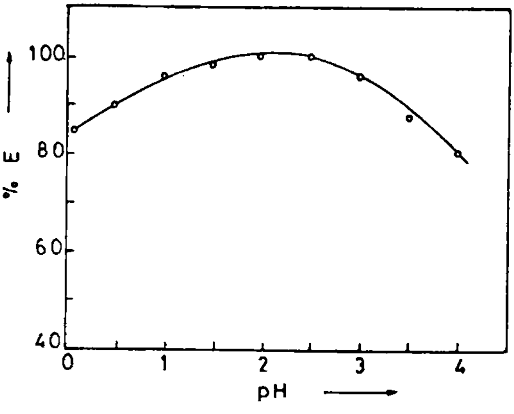

FIGURE 3.

tions are adequate for complete extraction. A 0.001 *M* solution can be used, but the time of equilibration required for complete extraction is high.

Effect of Diverse Ions

To examine the effect of diverse ions on extraction determinations of Mo(VI), 157.5 μg of molybdenum solution was extracted in the presence of varying amounts of diverse ions. The tolerance limit was taken at the amount required to cause ±1.5% error in molybdenum recovery. The

TABLE 2

Effect of Diverse Ions on Extraction of 157.5 μg of Mo(VI) in 25 ml 0.01 *M* OTMBHA Solution in Isoamyl Alcohol

Ion	Ion added as	Weight of compound added (μg)	Absorbance
		Cations	
UO_2^{2+}	$UO_2(NO_3)_2$	900	0.605
Cu^{2+}	$CuSO_4$	1,500	0.600
Ni^{2+}	$NiSO_4$	3,000	0.603
Zn^{2+}	$ZnSO_4$	3,000	0.600
Cd^{2+}	$CdSO_4$	3,000	0.600
Hg^{2+}	$HgCl_2$	3,000	0.605
Pb^{2+}	$(CH_3COO)_2Pb$	2,000	0.600
Ca^{2+}	$CaCl_2$	5,000	0.605
Ba^{2+}	$BaCl_2$	5,000	0.595
Sr^{2+}	$SrCl_2$	6,000	0.600
Be^{2+}	$BeSO_4$	2,000	0.600
Mg^{2+}	$MgSO_4$	6,000	0.605
Co^{2+}	$CoSO_4$	1,500	0.595
Mn^{2+}	$MnCl_2$	1,500	0.600
Sn^{2+}	$SnCl_2$	1,600	0.605
Cr^{3+}	$Cr_2(SO_4)_3$	1,600	0.600
W^{6+}	Na_2WO_4	1,400	0.600
La^{3+}	$La(NO_3)_3$	6,000	0.605
Sc^{3+}	$Sc(NO_3)_3$	6,000	0.600
Fe^{3+} [a]	$Fe(SO_4)_3$	6,000	0.595
V^{5+} [a]	$(NH_4)_2VO_3$	6,000	0.600
Ce^{3+} [b]	$Ce_2(SO_4)_3$	5,000	0.605
		Anions	
EDTA	Sodium EDTA	>10,000	0.600
Cl^-	NaCl	>10,000	0.605
Br^-	KBr	>10,000	0.595
F^-	NaF	>10,000	0.595
Phosphate	Na_2HPO_4	>10,000	0.600
Oxalate	$Na_2C_2H_2O_4$	>10,000	0.600
Borate	Na_3BO_3	6,000	0.605
Ascorbate	Sodium ascorbate	>10,000	0.600

[a] In presence of ascorbic acid as masking agent.

[b] In presence of EDTA as masking agent.

TABLE 3

Analytical Data on Extraction of Mo(VI)

Mo(VI) (μg/25 ml of organic extract)	Mo(VI) found (μg)	Error (%)	Standard deviation, σ
4.00	4.00	0.00	0.00
8.00	8.01	+0.01	0.01
10.00	10.00	0.00	0.01
50.00	49.99	−0.01	0.01
75.00	75.01	+0.01	0.02
100.00	100.02	+0.03	0.03
150.00	149.99	−0.01	0.03

results are presented in Table 2. It is seen that tolerance limits for many ions, including tungsten and chromium, the two metals included in Group VIB of the periodic table along with molybdenum, are very high. Also, molybdenum can be separated from many metals associated with nuclear fuels or fission products, e.g., cobalt, cadmium, lead, and the rare earths.

Analytical Data

To test the reliability of the present method, different amounts of molybdenum were extracted and determined. The data given in Table 3 show that there is excellent agreement in the experimental values.

DETERMINATION OF MOLYBDENUM IN STEELS

The British Chemical Standard Sample No. 64 B, containing 4.95% molybdenum in the presence of iron, vanadium, tungsten, and chromium, was dissolved in aqua regia, freed from nitric acid by treating with concentrated sulfuric acid, and dissolved in water. It was then rendered ammoniacal to dissolve any precipitated tungsten or molybdenum. Insoluble matter was filtered off, the pH of the solution was adjusted to 1.5 to 2.5, and molybdenum was extracted and determined as described above. Six determinations yielded the value 4.97 ± 0.02% of molybdenum.

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