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ATOMIC ABSORPTION SPECTROMETRIC MICRODETERMINATION OF TUNGSTEN (VI) IN ALLOYS AND ENVIRONMENTAL SAMPLES AFTER EXTRACTIVE SEPARATION WITH A HYDROXAMIC ACID INTO MIBK

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Tungsten (VI) was selectively extracted from 2–8 M HCl or 15–20 M H₂SO₄ media with N-p-methoxyphenyl-2-furylacrylohydroxamic acid (MFHA) in methyl isobutyl ketone (MIBK) and determined atomic absorption spectrometrically at 400.9 nm employing nitrous oxide-acetylene flame. The method was significantly more selective and sensitive than the prevailing methods for tungsten (VI) based on flame-AAS, and was successfully applied to the trace analysis of the metal in alloys, ores, plant tissues, animal tissues, and freshwaters. MFHA was chosen from amongst eleven new hydroxamic acids.

KEY WORDS: Tungsten, environment, analysis, AAS, extraction, hydroxamic acids.

INTRODUCTION

Tungsten in the environment

Tungsten is a trace element; its average abundance in crustal material lies between 0.5 and 2.0 ppm.¹ It is considered a strategically important metal because in some of its industrial and military applications it has no satisfactory substitute.² It is extensively used in making high-speed tool steel and other alloys. In addition, it is used in filaments for X-ray tubes, radio tubes, and light bulbs; in pigments; and in water proofing textiles. The abundance of tungsten in the earth's crust makes it a likely micro-constituent of animal and plant tissues but reports on this aspect are very few. Mosier and Nishi³ found tungsten levels ranging from 5 to 100 ppm (dry weight basis) in the Rocky Mountain trees, and Brooks⁴ gave 0.5 ppm as the likely concentration in plant ash.

Tungsten toxicity

According to Beliles,⁵ tungsten is absorbed to some extent from the gastro-

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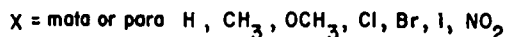
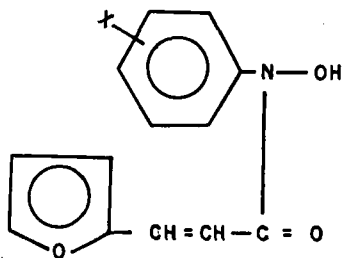


Figure 1 N-Phenyl-2-furylacrylohydroxamic acid and its analogues employed in the present study.

intestinal tract and retained largely in the bone, although smaller amounts have been assayed in the spleen, liver and kidney. The toxicity of tungsten compounds varies depending on the salt, and is manifested by nervous prostration, diarrhea, coma, and death due to respiratory paralysis.

The physiological significance of tungsten has not been investigated in detail. In a study on rats,⁵ the addition of soluble tungsten to the diet reduced the mortality and liver lesions characteristic of high levels of selenium intake. Increased tungsten intake also decreased molybdenum deposition in the livers of rats, and reduced intestinal xanthine oxidase. Sufficient amounts of tungsten caused molybdenum deficiency. This report on the interaction between molybdenum and tungsten in biological systems, the similarity in the chemistry of molybdenum and tungsten, the togetherness in their occurrence in minerals and soils, and the well-established biological significance of molybdenum, warrant more extensive studies on the occurrence of tungsten in animals, plants, waters and minerals, and on the possible biological significance of the metal, especially in relation to the availability and fate of molybdenum.

THE PRESENT METHOD

We have recently introduced N-phenyl-2-furylacrylohydroxamic acid (PFHA) and its analogues as sensitive and selective reagents for several metal ions, including palladium,⁶ vanadium,⁷ titanium,⁸ niobium,⁹ germanium,¹⁰ and molybdenum.¹¹ In the present investigation the hydroxamic acids were explored for the extractive separation and atomic absorption spectrometric determination of tungsten (VI). It was found that the hydroxamic acid solutions in methyl isobutyl ketone (MIBK) selectively extracted tungsten from 2–8 M hydrochloric acid or 15–20 M sulphuric acid media. The metal was determined atomic absorption spectrometrically by aspirating the extract into nitrous oxide-acetylene flame and measuring the absorbance at the 400.9 nm resonance line. Of the 11 hydroxamic acids studied, N-p-methoxyphenyl-2-furylacrylohydroxamic acid (Figure 1) was the most selective

and its tungsten chelate in MIBK gave the highest absorbance. The sensitivity of the present method (0.004 ppm) is significantly higher than the most sensitive flame-AAS method for tungsten reported so far (sensitivity 0.5 ppm).^{12,13} The method is also more sensitive than the "best" methods for tungsten based on atomic emission spectroscopy (sensitivity 0.2 ppm)¹² and atomic fluorescence spectroscopy (sensitivity 2.0 ppm).^{12,13} The method is also highly selective and was applied to the determination of tungsten in alloys and environmental samples.

Tungsten has been determined by AAS with high-temperature flames, but the sensitivity of the determination is rather poor due to the formation of thermally stable oxides in the flame.^{12,13} As a result, the direct determination is usually limited to concentrations above 1%.¹⁴⁻¹⁶ In addition to the low sensitivity serious interferences are encountered in analyses of many samples.¹⁵⁻¹⁷ To remove these drawbacks, tungsten has been separated by extraction with methyltricaprylammonium chloride,¹⁸ toluene-3,4-dithiol,¹⁹ α -benzoinoxime²⁰ and tri-n-octylamine oxide,²¹ when concentrations below 1% are determined. Sometimes solvents unsuitable for aspiration into flames have been used.^{19,21}

EXPERIMENTAL

Reagents and apparatus

All chemicals were of guaranteed reagent or equivalent grade unless otherwise specified. Water was deionised and doubly distilled.

Hydroxamic acids were synthesised by coupling the *para* or *meta* substituted phenylhydroxylamines with the oxychloride of furan-2-acrylic acid by the general method of Tandon and Bhattacharyya.²² The acids were repeatedly crystallised from benzene to constant, sharp, melting points and were characterised by elemental analysis, IR and UV spectroscopy, as detailed elsewhere.²³ Hydroxamic acids were employed as 0.3% (3 g l⁻¹) solutions in MIBK.

A stock solution of tungsten (1 mg ml⁻¹) was prepared by dissolving 1.261 g of pure tungsten trioxide, previously ignited at 750°C, in 25 ml of 2 M sodium hydroxide and diluting with water to 1 l. Solutions of other metals were prepared by dissolving the pure metals in hydrochloric acid.

The pH adjustments were done with Radiometer model PHM 29 and Industrial Electronics Corporation model 092 pH meters after precalibration with standard buffers of pH 4 and 9. For AAS studies, the Instrumentation Laboratory model IL 551/951 instruments, equipped with hollow cathode lamps for tungsten were used; the acetylene and nitrous oxide flow-rates were 6.21 min⁻¹ and 11.81 min⁻¹, respectively. A 0.48 × 40 mm slit burner was used. The height of the red zone of the flame was about 60 mm during nebulization of the tungsten-MFHA-MIBK extract. The height of the beam axis above the burner orifice was 10 mm. The tungsten hollow-cathode lamp was powered at 40 mA; wavelengths of 255.1 nm (spectral slit width 0.24 nm) and 400.9 nm (slit width 0.68 nm) were used. Scale expansion (3-5X) was done as required.

Analytical procedure

To the sample solution (25 ml) containing 10–75 μg tungsten (VI), taken in a 60 ml separating funnel, sufficient hydrochloric or sulphuric acid were added to make the sample 2–8 M in HCl or 15–20 M in H_2SO_4 . To it 10 ml of 0.3% MFHA solution in MIBK was added and the contents shaken vigorously for 1 minute. After phase separation the organic layer was drained off and its tungsten content was determined by AAS at the 400.9 nm line using the MFHA-MIBK reagent solution as blank.

RESULTS AND DISCUSSION

Measuring conditions

The efficiency of the atomization of the AAS flame increases with the reducing properties of the flame, but an increase in the fuel flow-rate above the specified value leads to excessive deposition of carbon at the edges of the slit. The maximum of the signal dependence on the beam height is rather sharp (Figure 2) and its position changes little on variation of the fuel-to-oxidant ratio; consequently, adjustment of the optimum flame is easy. All measurements were done at 400.9 nm because at 255.1 nm the signal-to-noise ratio was less favourable.

Choice of extracting solvent

Benzene, chloroform, carbon tetrachloride, and MIBK were tried as extracting solvents. Of these MIBK had the most favourable effect on the sensitivity of the method. Chlorinated solvents were especially unsuitable; they resulted in low sensitivity and produced pungent gases in the flame. In our earlier studies too,^{8–11} MIBK had proved to be the ideal carrier solvent in the AAS analysis; similar observations have been made by others.^{24,25}

Enrichment studies

Aqueous solutions of various volumes ranging from 10 to 500 ml, each containing a fixed amount—70 μg —of tungsten were extracted with 10 ml of MFHA-MIBK reagent solutions and analysed for tungsten following the present method. The studies revealed that the MFHA-MIBK system is capable of extracting tungsten quantitatively from aqueous phase up to 25 times the volume of the organic phase. The present method is therefore capable of enriching tungsten from very low levels.

Calibration curve and sensitivity

The calibration curve, passing through the origin, was linear in the range 0–

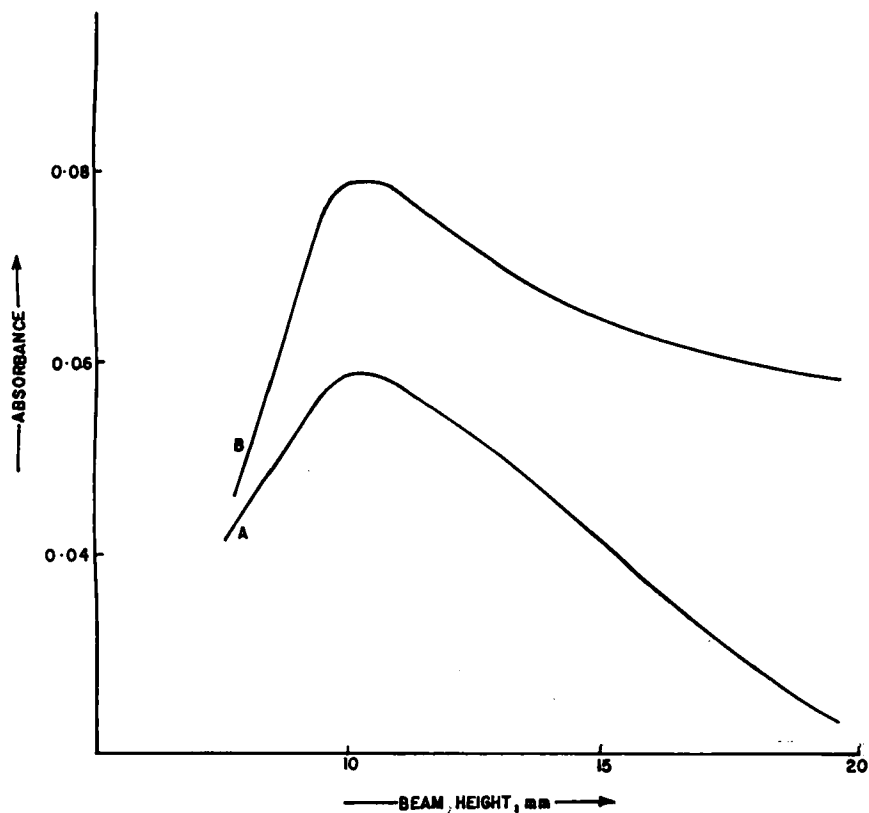


Figure 2 Effect of the height of beam axis on the absorbance.

9.5 ppm tungsten in the organic phase. The sensitivity of the method, defined as the concentration of tungsten causing 1% absorption,²⁶ was 0.1 ppm. The limit is enhanced to 0.004 ppm in the aqueous phase as a result of the 25-fold enrichment possible by the extraction system.

Optimisation of the MFHA concentration

A 0.3% (3 g l^{-1}) solution of MFHA in MIBK was optimum for the quantitative extraction of tungsten (VI). Higher reagent concentrations did not cause any significant improvement in the extraction efficiency, while lower reagent concentrations necessitated longer equilibration times. MFHA concentrations lower than 0.05% led to incomplete extraction of tungsten even after prolonged equilibration.

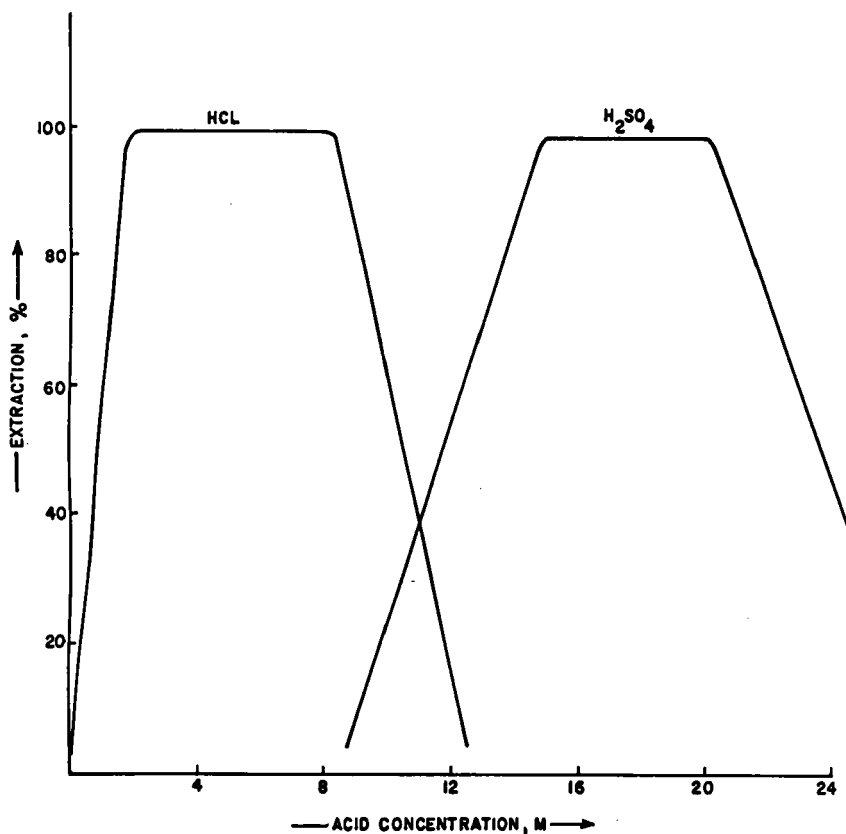


Figure 3 Extraction of tungsten (VI) by MFHA in MIBK as a function of the strength of HCl and H₂SO₄.

Effect of shaking time

An equilibration time of 1 minute was sufficient for the complete extraction of tungsten (VI) with a 0.3% MFHA solution in MIBK. Shorter shaking times led to incomplete extraction while no advantage accrued when the shaking was prolonged beyond 1 minute.

Effect of diverse ions

The effect of diverse ions on the determination of tungsten (VI) was studied using the recommended procedure. The tolerance limit was set at the concentration above which the foreign ion caused more than $\pm 2\%$ relative error in the tungsten

Table 1 Cations and anions tolerated in the determination of 70 μg of tungsten (VI) in 25 ml sample

<i>Foreign ion</i>	<i>Tolerance limit, μg</i>
Li(I), Na(I), K(I), Rb(I), Cs(I), chloride, bromide, iodide, nitrate, sulphate	... > 500,000
Be(II), Ca(II), Ba(II), Sr(II), Mg(II), Cu(II), Ni(II), Co(II), Fe(III), ^a Zn(II), Mn(II), Mg(II), Cd(II), Pb(II), phosphate	... 50,000
As(V), Sb(V), Bi(III), Sn(II), Sn(IV), Al(III), acetate	... 10,000
Mo(VI), Ti(IV), Zr(VI), Hf(VI), Nb(V), U(VI), Th(IV), Ce(IV)	... 5,000

^aHigher concentrations of iron can be removed by extracting the sample with 0.1 M MFHA in MIBK at pH \sim 1.5 prior to the extraction of tungsten.

Table 2 Determination of tungsten in alloy and environmental samples

<i>Sample</i>	<i>Tungsten present (certified value)</i>	<i>Tungsten added</i>	<i>Tungsten found (average of ten determination)</i>	<i>Standard deviation</i>
Tungsten-molybdenum ore (CANMET, ^a MP-2)	0.65 % 0.65 %	nil 1.000 %	0.639 % 1.643 %	0.063 0.131
Wolframite	— —	nil 5.000 %	53.96 % 59.03 %	1.65 2.04
Scheelite	—	nil	47.66 %	1.87
Alloy steel (ECRM ^b 112-1)	1.78 %	nil	1.804 %	0.113
Alloy steel (ECRM ^b 210-1)	1.54 %	nil	1.57 %	0.097
Legume (<i>Mimosa pudica</i>)	— —	nil 1.00 ppm	0.71 ppm ^c 1.69 ppm ^c	0.04 0.07
Liver of Squirrel	— —	nil 1.00 ppm	2.04 ppm ^c 3.05 ppm ^c	0.12 0.17
River water	— —	nil 1.50 ppm	nil ^d 1.47 ppm	— 0.05
Pond water	— —	nil 1.50 ppm	nil ^d 1.48 ppm	— 0.07

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^cIn samples dried at 120 °C.

^dBelow the detection limit of the present method.

recovery. The results (Table 1) indicate that the present method has a high degree of tolerance for the anions and cations commonly found with tungsten in alloys and environmental samples.

DETERMINATION OF TUNGSTEN IN ORES, ALLOYS, BIOLOGICAL MATERIALS AND NATURAL WATERS

The ores were dissolved by sodium carbonate fusion.¹⁶ The alloy samples were treated as described by Ghose and Kharat.²⁷ The plant tissue, animal tissue and water samples were processed as detailed by us elsewhere.⁶⁻¹¹ The results of the replicate analysis are presented in Table 2. To make sure that matrices are not influencing the analysis, tungsten was determined with and without standard addition. The results indicate the reliability of the present method.

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