

# Determination of Tungsten in Ores and Concentrates by Atomic Absorption Spectrometry: Suppression of Atomisation Interferences from Calcium

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A simple and rapid method for the determination of tungsten in ores and concentrates by atomic absorption spectrometry is described. A dinitrogen oxide - acetylene flame was used and the absorbance was measured at 400.9 nm. The samples were decomposed using fused potassium hydrogen sulphate, which was found to be a suitable flux for opening tungsten minerals. The potassium hydrogen sulphate also proved to be a powerful enhancing agent for the tungsten absorbance signal while eliminating many reported interferences. Eighteen elements were examined for interferences and only calcium was found to interfere seriously when present in concentrations greater than 0.1 mg per 100 ml. The depressive effect of calcium could be easily suppressed and the absorbance signal wholly restored to the original level by the addition of a sodium silicate solution such that the minimum ratio of the concentration of Si : Ca was 1.5 : 1. The method has been applied to the determination of tungsten in wolframite, scheelite, wolframite - cassiterite and heavy mineral stream concentrate samples.

**Keywords:** Tungsten determination; atomic absorption spectrometry; calcium interferences; ores; concentrates

In this laboratory the determination of tungsten as a major constituent in ores and concentrates is carried out by using a classical gravimetric method<sup>1</sup> involving the precipitation of tungstic acid with cinchonine followed by subsequent ignition to tungsten trioxide. For samples containing low levels of tungsten, the spectrophotometric method based on the extraction of a tungsten - dithiol complex into amyl acetate<sup>2</sup> is used. These procedures are time consuming, tedious and unsuitable for large numbers of samples. In addition, they are subject to interferences, particularly from niobium, tantalum, titanium and molybdenum in the former instance and from molybdenum in the latter.

In general, atomic absorption spectrometric methods for the determination of tungsten have poor sensitivity<sup>3</sup> and suffer from interferences<sup>4,5</sup> by a large number of cations. Various techniques<sup>4,6-10</sup> have been developed to overcome these limitations. Recently, Roy and Das<sup>6</sup> determined tungsten in rocks and minerals by the chelate extraction of tungsten with *N*-benzoylphenylhydroxylamine in toluene followed by atomic absorption spectrometry. Edger<sup>5</sup> and Rao<sup>7</sup> *et al.*<sup>11</sup> used sodium sulphate and potassium persulphate, respectively, for the dual purpose of enhancing the tungsten absorbance signal and to act as releasing agents in the atomic absorption spectrometric determination of tungsten in alloys, ores and concentrates. Spreng and Prager<sup>12</sup> determined tungsten in ores and concentrates using sodium carbonate fusion followed by the addition of sodium sulphate to eliminate interferences.

This paper describes a simple and rapid atomic absorption spectrometric method for the determination of tungsten in ores and concentrates using potassium hydrogen sulphate as a flux for opening up the sample and to enhance the tungsten absorbance signal and release it from interferences. Eighteen cations tested at various concentrations were found not to interfere in the determination. However, calcium in concentrations greater than 0.1 mg per 100 ml very seriously depressed the tungsten absorbance signal. It was found that the absorbance depression by calcium could be completely eliminated and the absorbance restored to its original value by the addition of a sodium silicate solution.

## Experimental

### Apparatus

A Varian Techtron Model AA 875 atomic absorption spectrometer, equipped with a 6-cm dinitrogen oxide - acetylene burner was used for all measurements. A standard hollow-cathode tungsten lamp was used as a line source. A reducing fuel-rich dinitrogen oxide - acetylene flame was used in all absorbance measurements with the dinitrogen oxide and acetylene flows set at 24 and 88, respectively. These settings are equivalent to flow-rates of 10 and 5.5 l min<sup>-1</sup>, respectively, according to the manufacturer's operating manual. The aspiration rate was 6 ml min<sup>-1</sup> and the absorbance read-out integration time was 2 s. Other conditions were: lamp current, 20 mA; wavelength, 400.9 nm; spectral band pass, 0.5 nm; and burner height, 10 mm.

### Reagents

**Tungsten standard solution**, 1000 µg ml<sup>-1</sup>. Prepared by fusing 0.6305 g of Specpure tungsten trioxide (WO<sub>3</sub>) (Johnson Matthey Chemicals) with 5 g of sodium hydroxide over a Bunsen burner flame in a platinum crucible. The melt was dissolved in water and accurately diluted to 500 ml with distilled water.

**Calcium solution**, 1 mg ml<sup>-1</sup>. Prepared by dissolving 1.38 g of CaCl<sub>2</sub> (Merck Chemicals) in distilled water and diluting to 500 ml.

**Sodium silicate solution**, 1% m/V. Prepared by dissolving 12.7 ml of sodium silicate solution (BDH Chemicals) of density 1.57 g ml<sup>-1</sup> in distilled water and diluting to 2 l. On standardisation the solution was found to contain 1.49 mg ml<sup>-1</sup> of Si.

**Tartaric acid solution**, 10% m/V. Prepared by dissolving 50 g of (+)-tartaric acid (AnalaR grade) in distilled water and diluting to 500 ml.

**Fused potassium hydrogen sulphate, solid**. Prepared by heating potassium hydrogen sulphate (KHSO<sub>4</sub>, pro analysi, Merck Chemicals) over a Bunsen burner flame in a silica dish until completely melted. The solid was cooled, broken into small pieces using a pestle and mortar and was stored in an air-tight bottle. Water was removed in order to obtain a quiet fusion without any loss of sample through spattering.

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## Calibration Graph

Pipette 5, 10, 15, 20, 25 and 30 ml of the tungsten standard solution into a series of 100-ml calibrated flasks. Add 10 ml of 10% tartaric acid solution to each flask followed by 5 ml of potassium hydrogen sulphate solution (containing 1 g of  $\text{KHSO}_4$ ). Dilute accurately to the mark with distilled water and prepare a blank in the same manner. These solutions are then aspirated into the spectrometer in the absorbance mode under the described conditions. A typical calibration graph is shown in Fig. 1.

## Procedure

### Determination of tungsten in ores and concentrates

Accurately weigh 0.1–0.25 g (depending on the tungsten content) of the finely ground sample into a silica crucible. Fuse the sample over a Bunsen burner flame with 1 g of fused potassium hydrogen sulphate for about 30–40 min. Start with a very low flame until all the potassium hydrogen sulphate has melted and then slowly increase the intensity of the flame to medium strength. After fusion and cooling, pour 10 ml of 10% tartaric acid solution into the crucible. The tartaric acid prevents the precipitation of any tungsten and other elements. With the lid on, carefully warm the contents of the crucible on a thin asbestos sheet on a hot-plate to dislodge the cake and occasionally stir the cake with a glass rod to help dislodge it. Transfer the contents of the crucible into a 100-ml beaker with distilled water and warm over the hot-plate to dissolve the cake completely. Add a little paper pulp and filter (Whatman No. 40, 9 cm) into a 100-ml calibrated flask. Wash the beaker and the residue with distilled water. Dilute to the mark and measure the absorbance under the described conditions.

For samples of unknown composition which are suspected to contain calcium, a rough determination of the calcium content is required. This is to permit the addition of a suitable volume of 1% sodium silicate solution to the sample solution in order to obtain the minimum ratio of Si:Ca required (1.5:1). For scheelite concentrates ( $\text{CaWO}_4$ ), take a suitable aliquot from the 100-ml sample solution and dilute to the desired volume after adding the appropriate amount of sodium silicate, potassium hydrogen sulphate and tartaric acid solutions. The sodium silicate solution should be added to give a Si:Ca ratio of 1.5:1, and the other two reagents should have concentrations adjusted to match the calibration standards. Scheelite samples from a particular source usually show no great variation in the calcium content. Hence, if the calcium content of one sample is known, it is possible to approximate its concentration in other samples. If approximation is not possible, pre-analysis for calcium is required.

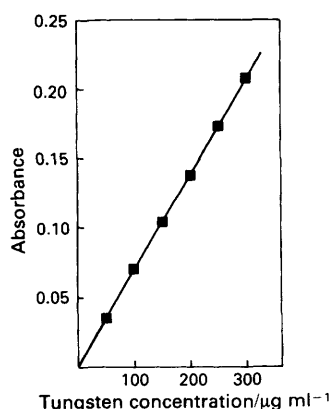


Fig. 1. Typical calibration graph for tungsten. Correlation coefficient = 0.9999. Regression equation:  $y = 0.0007x - 0.0001$

## Results and Discussion

### Enhancement Effect

At the  $100 \mu\text{g ml}^{-1}$  tungsten level, the addition of potassium hydrogen sulphate raised the absorbance reading from 0.030 to 0.069. This was an enhancement of about 130% compared with the 46% enhancement at the  $100 \mu\text{g ml}^{-1}$  tungsten level obtained by Edger<sup>5</sup> using sodium sulphate in acidic medium at 255.1 nm and the 75% enhancement obtained at the  $400 \mu\text{g ml}^{-1}$  tungsten level obtained by Raoot *et al.*<sup>11</sup> using potassium persulphate in alkaline medium at 400.9 nm. Under our experimental conditions, it was observed that potassium persulphate gave an improvement of about 120% in the  $100 \mu\text{g ml}^{-1}$  tungsten absorbance signal. The enhancement in absorbance for other tungsten concentrations can be seen in Fig. 2.

The general enhancement of the tungsten absorbance signal by sodium sulphate, potassium persulphate and potassium hydrogen sulphate seems to suggest that the sulphate anion is one of the necessary and preferential enhancing agents. Tests were carried out using sulphuric acid or potassium chloride in place of potassium hydrogen sulphate. It was found that sulphuric acid gave an enhancement equal to that given by potassium hydrogen sulphate, whereas the enhancement obtained with potassium chloride was much lower (Fig. 2). Hence the sulphate anion is a better enhancing agent than the potassium cation. Further tests were carried out using inorganic sulphate salts such as  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{LiSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  and  $\text{K}_2\text{SO}_4$  in amounts giving a sulphate concentration equal to that given by 1 g of  $\text{KHSO}_4$ . It was found that all these salts enhanced the signal of the  $100 \mu\text{g ml}^{-1}$  tungsten solution to a level similar or equal to that given by potassium hydrogen sulphate. One possible explanation of this phenomenon is similar to that advanced by Price<sup>13</sup> for the enhancement of the rhodium signal. Under the reducing conditions of the dinitrogen oxide - acetylene flame, some of the sodium tungstate is reduced to tungsten metal, which has a boiling-point of greater than  $5900^\circ\text{C}$ . Such a high vaporisation temperature is not achieved in a dinitrogen oxide - acetylene flame, thus leading to incomplete atomisation. In the presence of sulphate anions, the formation of metallic tungsten clots is prevented. A reaction between the free tungsten atoms and the solid solution of sulphate particles may occur. As the solid solution is vaporised in the flame, the tungsten atoms are released as an atomic vapour.

In this work we used 1 g of potassium hydrogen sulphate as a standard amount but the addition of 0.5 or 2 g of potassium hydrogen sulphate had no adverse effect on the tungsten absorbance. The presence of 10 ml of 10% tartaric acid also had no adverse effect.

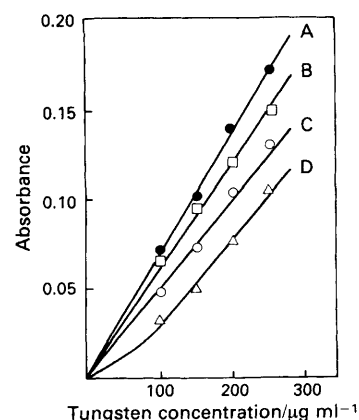


Fig. 2. Effect on tungsten absorbance signal of: A, 1% *m/V* potassium hydrogen sulphate or 0.4% *V/V* sulphuric acid; B, 0.1% *m/V* potassium persulphate; C, 0.57% *m/V* potassium chloride; and D, direct dilution from tungsten stock solution

Interferences

Eighteen elements were investigated for interference effects at various concentrations (Table 1). It was observed that in the presence of potassium hydrogen sulphate as a releasing agent, only calcium at concentrations greater than 0.1 mg per 100 ml interfered with tungsten by seriously depressing the absorbance signal (Fig. 3). A similar interference was observed by Spreng and Prager<sup>12</sup> who overcame the problem by fusing the sample with sodium carbonate yielding calcium carbonate which is insoluble in basic media. In this work it was found that the calcium interference could be completely eliminated and the tungsten absorbance wholly restored to its original value by the addition of a 1% sodium silicate solution such that the minimum ratio of Si to Ca was about 1.5:1 (Fig. 4). One explanation of the depression of the tungsten absorbance by calcium was the formation of a refractory calcium tungstate compound in the flame that inhibited the release of tungsten atoms. It is suggested that sodium silicate competes with tungsten for calcium atoms forming the more stable calcium silicate and releasing the tungsten as free atoms.

The effect of 18 selected cations on a 100 µg ml<sup>-1</sup> tungsten solution is shown in Table 1. These cations were selected on the basis that they are likely to be present in major or minor amounts in most samples containing tungsten. The tolerance limit listed in this table was set as the amount of foreign cation causing a ±2% error in the determination of tungsten. The salts used in this study were dissolved in a fixed volume of tartaric acid, if they were soluble. If they were insoluble in tartaric acid, the salts were fused with a fixed mass of fused

**Table 1.** Effect of foreign ions. Amount of W taken = 100 p.p.m. Some of these tolerance limits are not likely to be exceeded in routine analytical applications but they indicate the potentiality of the method in other applications

Foreign ion	Added as	Tolerance limit/mg
Al <sup>3+</sup>	AlCl <sub>3</sub> .6H <sub>2</sub> O	200
Ti <sup>4+</sup>	TiO <sub>2</sub>	200
Fe <sup>3+</sup>	Fe <sub>2</sub> O <sub>3</sub>	200
Mn <sup>2+</sup>	MnSO <sub>4</sub> .H <sub>2</sub> O	200
Nb <sup>5+</sup>	Nb <sub>2</sub> O <sub>5</sub>	100
Ta <sup>5+</sup>	Ta <sub>2</sub> O <sub>5</sub>	5
Mo <sup>6+</sup>	MoO <sub>3</sub>	200
Sb <sup>3+</sup>	Sb <sub>2</sub> O <sub>3</sub>	200
Ni <sup>2+</sup>	(CH <sub>3</sub> COO) <sub>2</sub> Ni.4H <sub>2</sub> O	50
Bi <sup>3+</sup>	Bi <sub>2</sub> O <sub>3</sub>	50
Mg <sup>2+</sup>	MgSO <sub>4</sub> .7H <sub>2</sub> O	200
Pb <sup>2+</sup>	Pb(NO <sub>3</sub> ) <sub>2</sub>	2
Co <sup>2+</sup>	(CH <sub>3</sub> COO) <sub>2</sub> Co.4H <sub>2</sub> O	200
Ag <sup>+</sup>	AgNO <sub>3</sub>	200
Zn <sup>2+</sup>	(CH <sub>3</sub> COO) <sub>2</sub> Zn.2H <sub>2</sub> O	50
Cu <sup>2+</sup>	CuSO <sub>4</sub> .5H <sub>2</sub> O	200
Sn <sup>2+</sup>	SnCl <sub>2</sub> .2H <sub>2</sub> O	100
Ca <sup>2+</sup>	CaCl <sub>2</sub>	0.1

**Table 2.** Determination of tungsten in ores and concentrates

Sample	Tungsten, %	
	Present method	Other methods
Wolframite . . . . .	29.7	29.8*
Scheelite . . . . .	59.5	59.4*
Scheelite rock . . . . .	1.00	1.00†
Wolframite - cassiterite (Sn, 60.7%) . . . . .	1.43	1.46†
Wolframite - cassiterite (Sn, 6.7%) . . . . .	0.69	0.71†
Stream concentrate . . . . .	0.88	0.86†
Stream concentrate . . . . .	0.40	0.37†

\* Gravimetric method, reference 1.  
† Spectrophotometric method, reference 2.

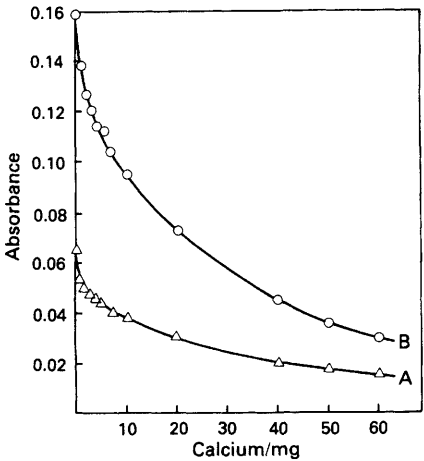
potassium hydrogen sulphate and subsequently dissolved in a fixed volume of tartaric acid. The concentrations of tungsten, potassium hydrogen sulphate and tartaric acid in all solutions analysed as part of this interference study were matched with the standard tungsten solution.

Analysis of Ores and Concentrates

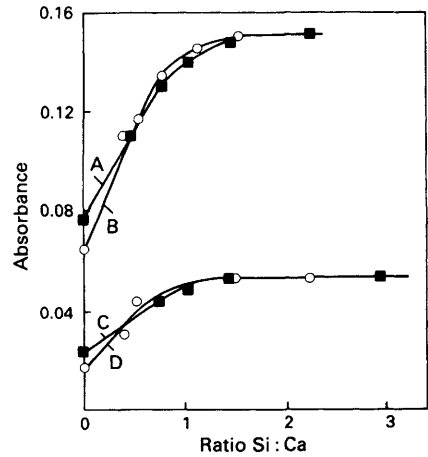
The proposed method has been applied to the analysis of a number of tungsten-bearing minerals, ores and concentrates and the results are as shown in Table 2. It can be seen that they agree well with those obtained by the spectrophotometric and classical gravimetric methods. Problems arising from a depression in absorbance by the presence of calcium, as occurs in samples containing scheelite, have been successfully eliminated.

Recovery Test

In order to test the validity of the proposed method, the standard additions method was used. Ten separate 0.10-g samples from a wolframite ore were accurately weighed and analysed by the proposed procedure. To each of five of these were added 10.000 mg of tungsten solution before diluting to the mark. Table 3 shows the recovery and precision results obtained. The recoveries ranged from 90 to 100% and the relative standard deviation of 4.2% shows that the proposed method has good reproducibility.



**Fig. 3.** Effect of calcium on tungsten absorbance. A, 100 p.p.m. W; B, 250 p.p.m. W



**Fig. 4.** Effect of silica on calcium interference in tungsten absorbance. A, 250 p.p.m. W, 10 mg of Ca; B, 250 p.p.m. W, 20 mg of Ca; C, 100 p.p.m. W, 10 mg of Ca; D, 100 p.p.m. W, 20 mg of Ca

**Table 3.** Determination and recovery of tungsten from 0.1 g of sample

W in sample/mg	W added to sample/mg	Total W found/mg	W recovered/ mg	Recovery, %
30.000	10.000	39.500	9.500	95
30.000	10.000	39.000	9.000	90
29.700	10.000	39.500	9.800	98
29.500	10.000	39.500	10.000	100
29.500	10.000	39.500	10.000	100
Mean			9.660 mg	
Standard deviation			0.422 mg	
RSD, %			4.2	

### Conclusion

Potassium hydrogen sulphate has been shown to be an effective flux and also a powerful enhancing and releasing agent in the determination of tungsten in ores and concentrates. If a sodium silicate solution is added to suppress calcium interferences, the method is free of interferences and is applicable to most tungsten ores and concentrates.

We thank the Director-General of the Geological Survey, Malaysia, for his permission to publish this paper.

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Paper A6/397

Received October 20th, 1986

Accepted December 15th, 1986