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THE DETERMINATION OF TUNGSTEN IN ORES, CONCENTRATES AND STEELS

by

G.H. Faye*, R.J. Guest** and R.C. McAdam*

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SYNOPSIS

Rapid and reliable procedures, all of which utilize a spectrophotometric finish, have been developed for the determination of tungsten in ores, concentrates and high-alloy steels. The proposed procedures have been applied to a variety of samples, including N.B.S. steel samples, covering a wide range of tungsten concentrations, and the results agree with those obtained by established but less convenient methods.

Ores and concentrates are decomposed by either an acid attack or a pyrosulphate fusion, depending upon the nature of the sample; steels are dissolved in an acid solution.

In the proposed procedures, tungsten is first reduced with stannous chloride under controlled conditions of temperature and acidity, and then complexed with thiocyanate. Tungsten may be determined directly by measuring the optical density of the coloured complex at 400 mμ, or, when interfering coloured substances are present, the complex may be extracted into a suitable organic solvent and its optical density measured. The optimum working range in the proposed method is from 0.05 - 1.00 mg of tungsten in the aliquot taken for analysis. The effect of a number of possible interferants is shown. Molybdenum, when present in conjunction with iron, causes high results, but this interference can be overcome by a prior extraction of the iron from a chloride medium with isopropyl ether.

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DOSAGE DU TUNGSTÈNE CONTENU DANS LES MINERAIS, LES CONCENTRÉS ET LES ACIERS

par

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RÉSUMÉ

Pour doser le tungstène contenu dans les minerais, les concentrés et les aciers fortement alliés, on a élaboré des procédés rapides et sûrs, qui se terminent tous par une étude spectrophotométrique. On a appliqué ces procédés proposés à une foule de spécimens, y compris des échantillons d'acier N.B.S., à teneurs très variées en tungstène. Les résultats de ces essais concordent avec ceux qu'on a obtenus à l'aide de méthodes classiques, mais moins commodes.

On décompose minerais et concentrés soit par l'attaque à l'acide soit par fusion au pyrosulfate, suivant la nature de l'échantillon; on dissout les aciers dans une solution acide.

Les méthodes proposées consistent à réduire d'abord le tungstène à l'aide de chlorure stanneux dans des conditions réglées de température et d'acidité, plus on le "complexe" à l'aide de thiocyanate. Le dosage du tungstène peut se faire directement en mesurant la densité optique du complexe coloré à 400 mμ, ou, quand des matières colorées interfèrent, on peut extraire le complexe à l'aide d'un solvant organique convenable et mesurer sa densité optique. L'intervalle expérimental optimum, dans la méthode proposée, varie de 0.05 à 1 mg de tungstène contenu dans la portion prise pour analyse. On montre l'effet produit par un certain nombre d'agents d'interférence possibles. Le molybdène associé au fer donne des résultats élevés, mais on peut surmonter cette interférence en extrayant d'abord le fer d'un milieu chloruré, à l'éther isopropyle.

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INTRODUCTION

The Mines Branch laboratories are frequently confronted with the necessity of determining tungsten in a wide variety of rocks, ores and mill products. The gravimetric method involving precipitation of tungstic acid with the aid of cinchonine has been tested here and gave erratic results. Previous workers (1, 2) have shown that this method may give low results because of incomplete precipitation, particularly on low-grade samples; also, that the method is subject to interference from other elements such as molybdenum, vanadium, tin, antimony, niobium and tantalum. Because of these problems, an alternative method was sought that would give accurate results and would be rapid and suitable for the routine analysis of low-grade ores and mill products.

Various colorimetric methods have been proposed for the determination of small quantities of tungsten, but the one most commonly used is based on the yellow thiocyanate complex formed by reduced tungsten in an acid solution. This method is preferred in ore and metallurgical analysis because other methods are subject to many interferences, and therefore, lengthy steps must be taken to isolate the tungsten before its estimation. The most common application of the thiocyanate method is for the determination of tungsten in steels. However, it has also been used by Sandell (3) for silicate rocks, and by Grimaldi and North (4) for low-grade tungsten ores.

Sandell's method was considered to be unsatisfactory for routine work in these laboratories because it is subject to interferences and involves many tedious steps. The method of Grimaldi and North, which involves reduction of tungsten with stannous chloride, was tested in these laboratories as it appeared to be the most suitable of those available. However, the results obtained were not reproducible, and, in addition, the recommended acid attack was not satisfactory for decomposing some types of samples.

Freund, Wright and Brookshier (5) obtained erratic results in determining tungsten in pure solutions by the stannous chloride-thiocyanate method and therefore undertook a systematic investigation of the reactions involved in the method. They studied the effect of free acid, chloride and chlorostannous ion concentrations and arrived at optimum conditions for reduction of tungsten and subsequent colour development.

This report describes the successful application of the procedure of Freund et al. (5) to the determination of tungsten in ores, concentrates and steels covering a wide range of tungsten concentrations. The results obtained by the proposed method agree favourably with those obtained by an X-ray fluorescence method for ores, and also with the Certificate values for certain National Bureau of Standards steel samples.

REAGENTS AND APPARATUS

Stannous Chloride Solution, 2 M - prepare by dissolving 113 g of stannous chloride dihydrate in concentrated hydrochloric acid and making up to 250 ml with the concentrated acid.

Potassium Thiocyanate, 20% - prepare by dissolving 20 g of potassium thiocyanate in 80 ml of water. This reagent should be prepared fresh daily.

Tartaric Acid Solution - prepare by dissolving 75 g of tartaric acid in 1 litre of water.

Stock Tungsten Solution - prepare by dissolving an accurately weighed quantity of $Na_2WO_4.2H_2O$ in water, followed by dilution to an appropriate volume. For example, 0.9 g of $Na_2WO_4.2H_2O$ dissolved in water and diluted to 1 litre gives a solution containing 0.5 mg of tungsten per ml. A suitable working solution is prepared from this stock by ten-fold dilution.

It has been found by experiment that $Na_2WO_4.2H_2O$ is as satisfactory a standard source of tungsten as tungstic acid dried at 110°C, and is more convenient to use.

Isopropyl Ether or Ethyl Acetate - reagent grade, peroxide free.

Spectrophotometer - Beckman Model "B".

PROCEDURE

Calibration Curve - prepare by taking aliquots of the standard tungsten solution through Procedure 3 given below. The working range of the curve is between 0.05 and 1.00 mg of tungsten in the aliquot taken for analysis.

1. Sample Decomposition

(a) Ores and Concentrates

(1) Acid Attack

This method of decomposition is recommended for samples containing less than 0.2% tungsten or for samples containing a comparatively high proportion of molybdenum.

To a 0.1000 - 2.000 g sample in a platinum dish, add approximately 1 ml of 85% phosphoric acid, 15 ml of 48% hydrofluoric acid, and 15 ml of concentrated hydrochloric acid. Allow the mixture to digest on the hot-plate until it has evaporated to a pasty consistency, cool, add 10 ml of 2N hydrochloric acid, and stir with a rubber policeman until the paste has dissolved. Filter the resultant solution through a fast paper into a volumetric flask of appropriate size and dilute to the mark with water.

(2) Fusion with Pyrosulphate

This method of decomposition is recommended for samples containing more than 0.2% tungsten, and also when the extraction of the tungsten thiocyanate complex (Procedure 4) is not contemplated.

Transfer a 0.1000 - 0.5000 g sample to a Vitreosil crucible containing 4 - 5 g of potassium pyrosulphate and mix well. Cover the mixture with a little more pyrosulphate and fuse over an open flame for approximately 5 minutes. After the fusion cake has solidified and cooled sufficiently, transfer the crucible and contents to a 400-ml beaker and dissolve the cake with 75 - 150 ml of 0.5 M tartaric acid on the hot-plate. Filter the resultant solution, wash the paper, and dilute to an appropriate volume with 0.5 M tartaric acid.

(b) Steels

Dissolve a 0.1000 - 1.000 g sample of the steel with 10 - 20 ml of phosphoric-sulphuric acid mixture, which is 15% of each acid by volume. Add concentrated nitric acid dropwise to decompose carbides, tungstides, etc.; then evaporate the solution to fumes of sulphur trioxide. When cool, transfer the solution to a suitable volumetric flask and dilute to the mark with water. Determine the tungsten content of an aliquot portion of this solution as in Procedures 3 plus 4 below.

2. Elimination of Interference Due to Molybdenum Plus Iron

After the sample has been evaporated to a pasty consistency in the presence of phosphoric acid in the case of ores (Procedure 1(a).(1)), or to fumes of sulphur trioxixe in the case of steels (Procedure 1(b)), cool to room temperature, add 20 ml of 12 N hydrochloric acid, and wash the solution into a 60-ml separatory funnel with 10 ml of water. Extract the solution three times with 15-ml portions of isopropyl ether and wash each extract twice with 2 - 3 ml portions of 8 N hydrochloric acid. Combine

the iron-free aqueous phase and the washings in a 250-ml beaker and warm on the hot-plate until any remaining isopropyl ether has been driven off. Cool the solution, transfer it to a volumetric flask, and dilute to an appropriate volume. Determine the tungsten content of the samples as in Procedures 3 and 4 below.

3. Colour Development

Use the following procedure when it is known that the sample solution does not contain elements that form coloured thiocyanate complexes in an acid solution or that themselves give coloured solutions.

Transfer an aliquot containing between 0.05 and 1.0 mg of tungsten to a 100-ml volumetric flask and dilute to approximately 15 ml with water. Add 10 ml of concentrated sulphuric acid, 20 ml of 12 N hydrochloric acid, and 5 ml of 2 M stannous chloride solution, with careful mixing after each addition. Place the flask in a boiling water bath for one hour, if the sample was decomposed by the acid attack (Procedure 1 (a).(1)); or for 10 minutes if the fusion method of decomposition was used (Procedure 1(a).(2)). Add 10 ml of water, mix, and finally cool the flask to 10 - 15°C. Next, add by pipette 10 ml of 20% potassium thiocyanate solution, dilute to volume, mix, and allow the sample solution to stand at room temperature for 10 minutes. Determine the optical density of the solution at a wavelength of 400 mμ against a reagent blank, and determine the tungsten content of the sample by reference to a calibration curve prepared by taking standard tungsten solutions through the above procedure.

4. Extraction of Tungsten Thiocyanate

Use the following procedure for sample solutions containing interfering coloured constituents and/or for samples expected to be very low in tungsten.

Transfer an aliquot of the tungsten thiocyanate solution prepared as in Procedure 3 above, to a 60-ml separatory funnel and then shake with peroxide-free isopropyl ether for 30 seconds. Ethyl acetate may be used instead of isopropyl ether; in such a case dilute the strongly acid solution one to four with water before extraction.

If the tungsten content of the tungsten thiocyanate solution is expected to be less than 0.05 mg of tungsten per 100 ml, extract a 50-ml aliquot with 5 ml of the organic solvent; with solutions of greater tungsten content, extract a 20-ml aliquot with 10 ml of the organic extractant.

After the phases have separated, discard the lower aqueous phase and measure the optical density of the extract at a wavelength of 400 mμ against a reagent blank. Determine the tungsten content of the sample by reference to a calibration curve prepared by taking aliquots of a standard tungsten solution through the colour-developing and extraction procedures. It should be noted that it is necessary to prepare a calibration curve for each organic extractant used.

EXPERIMENTAL

Reduction of Tungsten

Because the reduction of tungsten (VI) with stannous chloride is slow at room temperature, previous workers recommended that this step be carried out at elevated temperatures by boiling the sample solution directly (6), or by placing the reaction mixture in a boiling water bath (5).

Experiments with standard tungsten solutions were performed under a variety of conditions to determine the effectiveness of these methods of temperature control when the method of Freund et al.(5) was used for the reduction of the tungsten and for the subsequent formation of the coloured tungsten thiocyanate complex. In certain of these experiments the effect of phosphoric acid was also determined, as it was expected that this reagent would be present in sample solutions obtained by the acid attack on tungsten ores (Procedure 1 (a).(1)) and also on steels (Procedure 1(b)).

The results of these experiments are given in Table 1.

TABLE 1

Reduction of Tungsten under Various Conditions - Method of Heating, Time, Presence of Phosphoric Acid

Test	0.50 mg Tungsten Taken - Procedure 2			
	Boiling Water Bath	Direct Boiling on Hot-Plate	Conc. Phosphoric Acid (ml)	Tungsten Found (mg)
	Time in Minutes			
1	2	--	--	0.50
2	15	--	--	0.50
3	60	--	--	0.50
4	5	--	0.5	0.44
5	20	--	0.5	0.46
6	30	--	0.5	0.50
7	60	--	0.5	0.50
8	60	--	1.0	0.50
9	60	--	3.0	0.50
10	--	1	--	0.50
11	--	4	--	0.50
12	--	5	--	0.47
13	--	7	--	0.44
14	--	2	0.5	0.41
15	--	2	1	0.42
16	--	2	3.0	0.42

The results in Table 1 show that, in the absence of phosphoric acid, complete reduction of tungsten was achieved within 2 minutes using either method of heating the reaction mixture. However, when the sample solutions without phosphoric acid were boiled directly on the hot-plate for 5 minutes or more, low tungsten results were obtained (Tests 12 - 13).

In Tests 14 - 16, low tungsten values were obtained when synthetic sample solutions containing 0.5 - 3.0 ml of phosphoric acid were boiled directly on the hot-plate for 2 minutes.

It is evident from the results of Tests 4 - 9 that tungsten was not completely reduced in less than 30 minutes when sample solutions containing from 0.5 - 3.0 ml of concentrated phosphoric acid were heated in the boiling water bath.

The results given in Table 1 indicated that the most widely applicable method for reducing tungsten should involve heating the reaction mixture in a boiling water bath for 30 minutes. However, when these conditions were later applied to the analysis of solutions obtained by the acid attack of certain scheelite ores, occasionally a 30-minute heating period was found to give low and erratic results. In subsequent tests with similar sample solutions, highly reproducible results were obtained when the reduction period in the boiling water bath was extended to 60 minutes.

With solutions obtained from the pyrosulphate fusion of tungsten ore samples (which contained no phosphoric acid), a 10 minute

heating period in the boiling water bath gave reproducible results, and this is in agreement with the results of Tests 1 and 2 given in Table 1.

At the present time a satisfactory explanation cannot be offered for the effect of phosphoric acid on the reduction of tungsten under the conditions of the proposed procedures.

Extraction of Tungsten Thiocyanate Complex

Organic solvents have been used by Sandell (3) for extracting the tungsten thiocyanate complex. This technique was investigated in these laboratories, as it was considered that it would increase the sensitivity of the spectrophotometric aspect of the procedure, and would eliminate interference by coloured substances likely to be encountered in sample solutions derived from ores, concentrates and steels. The following solvents were tested for this purpose: n-amyl alcohol, cyclohexanol, ethyl acetate, butyl acetate, amyl acetate, a solution of tributyl phosphate in carbon tetrachloride, ethyl ether, and isopropyl ether. It was found that the thiocyanate complex could be extracted into all the solvents tested, although isopropyl ether was considered to be the most satisfactory because it separated cleanly from the aqueous phase and because the batch available was essentially peroxide-free. Many of the other solvents contained oxidizing agents (probably organic peroxides) and these gave extracts with low and variable optical densities when measured spectrophotometrically. Therefore, it is recommended that the particular solvent chosen

for the extraction step be examined for peroxides and purified, if necessary, before use (7, 8).

Determination of Tungsten in Presence of Foreign Substances

Because of the anticipated necessity for the determination of tungsten in sample materials containing phosphates and borates, a series of synthetic tungsten-bearing solutions containing various mixtures of these contaminants was prepared and analyzed for tungsten according to the procedure for colour-development given in Procedure 3 above. Table 2 gives the results of these experiments.

TABLE 2

Effect of Phosphates and Borates on Determination of Tungsten*

Tungsten Taken (mg)	Contaminants (mg)	Tungsten Found (mg)
0.30	350 sodium metaphosphate	0.30
0.30	350 " pyrophosphate	0.30
0.30	350 " tetraborate	0.30
0.30	100 " metaphosphate +50 " pyrophosphate	0.30
0.30	100 " metaphosphate +50 " pyrophosphate +100 " tetraborate	0.30

*Reduction in boiling water for 1 hour.

The results given in Table 2 indicate that, for the range

investigated, borates and phosphates and mixtures thereof do not interfere with the determination of tungsten by the stannous chloride-thiocyanate method.

Since molybdenum (4, 9), niobium (9), vanadium (7, 10) and titanium (4) have been reported as interferants in previous methods for tungsten, and because uranium, nickel, and cobalt form coloured thiocyanate complexes under some conditions, interference studies were conducted with these metals.

In separate tests, a known quantity of a solution of each of the foreign metals was added to an aliquot of the standard tungsten solution and the mixture was taken through the procedure used for the acid attack of ores. Each of the resultant sample solutions was analyzed for tungsten, by Procedures 3 and 4 above and the results of these tests are given in Table 3.

TABLE 3

Determination of Tungsten in Synthetic Solutions Containing Foreign Metals

0.25 mg Tungsten Taken	
Foreign Metal Present (mg)	Tungsten Found (mg)
4 Mo	0.25
20 Ti	0.25
40 Ni	0.25
20 U	0.25
20 Co	0.25
17.5 Nb	0.27
20.0 V	0.26

The results given in Table 3 show that, of the foreign metals investigated, only niobium and vanadium caused detectable interference in the determination of tungsten. However, it is apparent that, even when these metals are in large excess over tungsten, their interference is comparatively small and, therefore, few samples are likely to be encountered in which the presence of niobium and/or vanadium would constitute a problem.

Interference of Molybdenum

While working with synthetic solutions containing only tungsten and molybdenum, it was found that molybdenum caused no interference in the determination of tungsten even when present in twenty-fold excess over tungsten. However, when the proposed method was applied to the determination of tungsten in molybdenum-bearing steels, high values were obtained. In this work it was observed that the ether extract, which is ordinarily a greenish-yellow, was a deep orange in colour, indicating the presence of molybdenum(V) thiocyanate.

To investigate this problem further, a series of tests was conducted in which tungsten was determined in synthetic solutions containing known amounts of tungsten, molybdenum and iron, by the method given in Procedures 3 plus 4. The results of these tests showed that the interference due to molybdenum was dependent on the amounts of molybdenum and iron in the sample solution (Table 4).

The effect of iron on the formation of Mo (V) thiocyanate has been studied by Dick and Bingley (11). These workers postulated the formation of the complex $Mo_2^{III}\left[Mo^{V}O(CNS)_5\right]_3$ in the absence of iron and of $Fe^{II}\left[Mo^{V}O(CNS)_5\right]$ in its presence. The part of the molecule within the brackets is considered to be the chromogenic portion; therefore,in the absence of iron only part of the molybdenum forms a coloured species.

Under the conditions of the proposed method, it is presumed that in the absence of iron molybdenum is in the tervalent condition and forms a colourless thiocyanate complex (12) ; consequently it offers no interference in the determination of tungsten.

TABLE 4

Effect of Iron on Molybdenum Interference

Metals Present			Tungsten Found (mg)
Tungsten (mg)	Molybdenum (mg)	Iron (mg)	
0.25	4	none	0.25
0.25	4	10	0.26
0.25	4	25	0.27
0.25	4	50	0.27
0.50	10	50	0.56
0.50	10	100	0.57
0.50	10	150	0.62

The results given in Table 4 suggested that, if iron were removed from the sample solution prior to the determination of

tungsten, then satisfactory results might be obtained in the presence of molybdenum. To determine the suitability of this approach, a series of synthetic sample solutions containing known quantities of tungsten, molybdenum and iron was prepared and each sample was taken through the acid treatment for the decomposition of ores. Iron was removed from the sample solution by ether extraction from hydrochloric acid medium, and tungsten was then determined as above in Procedures 3 plus 4. The results of these tests are given in Table 5.

TABLE 5

Determination of Tungsten in Iron-Free Solution Containing Molybdenum

500 mg Fe Present Before Extraction		
Metals Present (mg)		Tungsten Found (mg)
Tungsten	Molybdenum	
0.25	none	0.25
0.25	5	0.25
0.25	10	0.26
0.25	20	0.26

The results given in Table 5 thus confirm that tungsten can be determined by the stannous chloride-thiocyanate method in the presence of a large excess of molybdenum without appreciable interference, provided that the bulk of any iron present is first removed.

Decomposition of Tungsten Ores

Of the several possibilities for decomposing tungsten ores, fusions with sodium peroxide or potassium pyrosulphate were studied, and also various acid attacks. Although fusion methods gave complete decomposition, difficulties were sometimes encountered when the tungsten thiocyanate complex was subsequently extracted with organic solvents. In the presence of large amounts of alkali metal salts introduced from the flux, the organic solvent and the sample solution tended to form an emulsion from which the coloured extract could not be easily separated. After fusions with sodium peroxide, silica occasionally precipitated in a gelatinous form in later steps and was difficult to remove by filtration. Also, it was thought that there might be some danger of losing tungsten by occlusion in the precipitated silica.

Pyrosulphate fusions were found to be satisfactory, especially with high-grade materials where small samples could be used and when extraction of the tungsten thiocyanate complex into an organic solvent was not required.

Since it was desired to retain the extraction procedure, experiments were conducted to find a means of decomposing tungsten ores that would not give a solution with a high concentration of dissolved salts. As tungsten forms soluble complexes with chloride, fluoride and phosphate, a mixture of the corresponding acids was

tested as a means of decomposing tungsten minerals. A number of samples of scheelite, wolframite and ferberite were ground to -200 mesh and were treated with a 1:1 mixture of 48% hydrofluoric acid:12N hydrochloric acid and 1-2 ml of syrupy phosphoric acid. The mixtures were allowed to digest on the hot-plate until they had evaporated to a paste of phosphoric acid, in order to drive off excess free fluoride. The samples were then taken up in dilute hydrochloric acid and the insoluble residues were recovered by filtration. Spectrographic analysis of the residues showed that, in all cases, at least 98% of the tungsten in the original sample was taken into solution by the mixed acid attack.

It was found that wolframite required a prolonged and repeated treatment with the acid mixture to achieve complete decomposition. It is considered, therefore, that for ores and concentrates containing this mineral the fusion decomposition with pyrosulphate would be more convenient.

Application to Ores and Steels

a) Ores

To determine its practicability, the proposed method was applied to a number of mill products containing tungsten in the form of scheelite. For comparison purposes certain of these samples were analyzed gravimetrically by double cinchonine precipitation (1), while others were analyzed by an X-ray fluorescence method using the silica dilution technique (13). The results of these analyses are given in Table 6.

TABLE 6

Determination of Tungsten in Mill Products - Comparison of Colorimetric, Gravimetric and X-ray Fluorescence Results

Test No.	Description of Sample	% Tungsten			
		Stannous Chloride-Thiocyanate		Gravimetric	X-ray Fluorescence*
		Procedure 3 (No extraction)	Procedure 4 (Extraction)		
1	Scheelite conc.	47.1	---	45.8	---
2	Head sample	1.58	1.56	1.17	---
3	Tailing	0.21	0.24		---
4	Scheelite conc.	9.8	---		9.5
5	" "	22.5	---		22.6
6	" "	28.5	---		28.6
7	" "	42.2	---		41.7
8	" "	52.3	---		53.0

In Tests No. 1-3, the samples were decomposed by the mixed acid attack.

In Tests No. 4-8, the samples were decomposed by pyrosulphate fusion.

*X-ray fluorescence results by Mrs. D.J. Reed, Mineral Sciences Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa.

Table 6 shows that the results obtained by the proposed method in Tests 4-8 are in excellent agreement with those obtained by the X-ray fluorescence method. It is also evident from Tests 2 and 3 that the tungsten results obtained by Procedures 3 and 4, with or without extraction of the tungsten thiocyanate complex, are concordant. In addition, Tests 1 and 2 show that the gravimetric results are lower than those obtained by the stannous chloride-thiocyanate method.

b) Steels

The proposed method was applied to the determination of tungsten in a number of National Bureau of Standards steel samples, by using Procedures 1(b) or 2 as above, and the results are given in Table 7. These steels are highly alloyed and contain one or more of the following elements: molybdenum, chromium, vanadium, nickel, and cobalt. Therefore, it was considered that these samples would provide an adequate test of the extraction procedure designed to eliminate potential interference due to coloured ions and to molybdenum.

TABLE 7

The Determination of Tungsten in N.B.S. Steels

N.B.S. Sample No.	N.B.S. Certificate Values		Tungsten Found (%)
	Molybdenum (%)	Tungsten (%)	
123a	0.12	0.11	0.11 (3)
155	0.039	0.517	0.51
153	8.39	1.58	1.57 (4)
134	8.68	1.82	1.89 (11)
132	7.07	6.28	6.24 (5)
50B	0.40	18.05	17.9 (7)

Figures in parentheses indicate number of replicate determinations on separate samples.
Samples 123a, 155 and 50B analyzed by Procedure 1(b).
Samples 153, 134 and 132 analyzed by Procedure 2.

Table 7 shows that the results obtained by the proposed method are in excellent agreement with the N.B.S. certificate values for tungsten; also,that tungsten can be determined reliably in the presence of a large excess of molybdenum.

From the replicate determinations run on samples 134 and 50B, the standard deviations were calculated to be 0.043% and 0.37% tungsten respectively.

SUMMARY

The stannous chloride-thiocyanate method for determining tungsten has been applied to the analysis of tungsten-bearing ores and steels. Methods of sample decomposition have been investigated and a new acid attack for ores has been developed. A procedure has also been devised for extracting the tungsten thiocyanate complex from solutions containing interfering coloured ions, at the same time permitting an increase in the sensitivity of the method for low-grade samples.

It is considered that the proposed procedures are applicable to a wide variety of ores and mill products, as well as steels and possibly other alloys. Although the method was developed for low-grade ores and mill products, it has been found superior to other chemical methods for high-grade tungsten concentrates.

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