GEOCHEMISTRY OF TUNGSTEN

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SCOPE AND CONTENTS:

Rock samples were collected in the tungsten enriched area of Salmo, B.C. These samples were to be analyzed for tungsten. Preliminary spectrographic and colorimetric orientation tests were carried out to find a suitable method for analysis of tungsten at the p.p.m. level, after a wet chemical pre-enrichment procedure. The colorimetric method was established for the simultaneous determination of W and Mo (Jeffery, 1959). A colorimetric method, recently developed by Chan and Riley (1967), was finally adopted since it appeared to be a reliable method because of the control carried out with a radioactive tracer. The application of this method however leads to results generally lower and without any trend, when compared to those obtained by the authors of the method. A loss of tungsten probably occurs during the procedure. Disagreement on the W contents of the new U.S.G.S. standard rocks as obtained by Chan and Riley (1967) was expressed by Johansen and Steinnes (1970). Further investigations on tungsten at the p.p.m. level are suggested using neutron activation.

ABSTRACT

Chan and Riley (1967) developed a colorimetric method for the determination of tungsten in natural waters and silicate rocks. Applied to silicate rocks this method contains the following stages: evaporation of silica with hydrofluoric acid, co-precipitation of tungsten and some other elements, with hydrous manganese dioxide and cation-exchange separation of vanadium, molybdenum and tungsten. When applying this method on standard solutions and the new U.S.G.S. standard rocks, the results obtained are lower than those suggested by the authors. The results obtained recently with neutron activation analysis of the same standard rocks by Johansen and Steinnes (1970), although different from the results of the present work, also disagree with Chan and Riley. The method was abandoned since a tungsten loss is believed to occur throughout the procedure.

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CHAPTER I

GENERAL ASPECTS ABOUT THE GEOCHEMISTRY OF TUNGSTEN

Tungsten, a transition element of the group VI B, together with chromium and molybdenum, occurs in economically interesting deposits mostly as:

Huebnerite	$MnWO_4$	(0-20 atomic % Fe)
Wolframite	$(Fe,Mn)WO_4$	(20-80 atomic % Fe)
Ferberite	$FeWO_4$	(80-100 atomic % Fe)
Scheelite	$CaWO_4$	

The wolframites, for example, contain impurities of niobium, tantalum and tin, but rarely scandium and titanium (Drouginine and Sobolevski, 1967), presumably because W^{6+} can substitute or be substituted by Nb^{5+} and Ta^{5+}. Therefore niobium-tantalum minerals may contain up to one percent (or more) tungsten.

As contrasted with tungsten deposits with a minimum content of 0.1% WO_3 for mining, tungsten generally occurs in much lesser amounts (p.p.m. range and less) in rocks. Its abundance, however, increases with acidity (quartz content), although tungsten contents usually are very low in quartz and felspars, i.e. often less than one p.p.m. (Jeffery, 1959; Ivanova, 1969).

The highest tungsten content in abundant minerals in igneous rocks occurs in micas (5-50 p.p.m.) but in altered granites near tungsten deposits muscovite can contain up to 500 p.p.m. (Jeffery, 1959; Ivanova, 1969). In accessory minerals tungsten shows concentrations of 10 p.p.m. and more in iron oxides and titanium minerals (Jeffery, 1959; Lyakhovich and Balanova, 1969).

Based on its distribution in meteorites, Mason (1966) calls tungsten a siderophile element, but he refers to it as a chalcophile element in the earth's crust.

Many reports have been published on tungsten ore deposits. On the contrary the few papers on tungsten as an element start usually with, for example, a statement like "The geochemistry of tungsten is poorly known." (Vinogradov, Vainshtein and Pavlenko, 1958). Moreover, the few existing data lead many times to controversies. According to Krauskopf (1970, p.74-E-1) pre-1946 analyses of tungsten "are almost certainly in error", "...owing to the use of unsatisfactory analytical techniques" (Chan and Riley, 1967, p.103).

Since then a few attempts have been made to contribute to a better knowledge of tungsten, firstly because it is economically a very important element, although a rather rare one, but also because it has been treated rather badly compared to other elements.

The most complete study has been done by P. G. Jeffery (1959), who analysed some 273 samples of rocks and minerals from all over Uganda. He reported a value of 1.4 p.p.m. as the terrestrial abundance of tungsten in granitic rocks, suggesting at the same time that further work should be done especially on other silicate rocks and carbonates.

Around the same period Vinogradov et al. (1958) presented analytical data on molybdenum and tungsten in igneous rocks as shown in Table 1.

Table 1. Average content of tungsten and molybdenum/tungsten ratio in different rock types (p.p.m.)

(After Vinogradov et al. 1958)

	Ultramafic	Mafic	Intermediate	Felsic
W-average	0.77	0.85	1.9	2.4
W-range	0.33-2.5	<0.6-1.6	1.4-3.3	1.9-3.3
Mo/W	0.29	2.5	0.56	0.7

These authors report an average tungsten content of the earth's crust of 2 p.p.m. Tungsten exceeds molybdenum 1.5 to 2 times on the average but mafic rocks appear to show a reversed tendency, if their data can be accepted.

In the sixties, most work on tungsten has been done using neutron-activation analysis. A few meteorites and tektites have been studied and also some standard rocks.

In the compilation of data on the rocks G-1 and W-1, Fleischer (1965, p.1276; 1969, p.78) gives the following data as shown in Table 2.

Fleischer (1965, p.1276) comments on these data that "no change is warranted", although no "recommended value" is given as is the case for other elements.

Table 2. Content of tungsten in G-1 and W-1 in p.p.m.

G-1	W-1	Method	Reference
0.47	0.46	Neutron activation	Ahrens & Fleischer (1960)
0.4	0.45	Neutron activation	Fleischer & Stevens (1962)
0.5 (av. of 4)	0.58 (av. of 5)	Neutron activation	Hamaguchi & others (1962)
<0.2	<0.2	Mass spectrometer	Brown & Worstenholme (1964)
0.4	0.30	Mass spectrometer	Taylor (1965)
<0.8	-	Optical spectrography	Ivanova (1966)

The only data on the new U.S.G.S. standards, compiled by F. J. Flanagan (1969, p.107) are the results obtained photometrically by Chan and Riley (1967, p.171). These data are given in Table 3.

Table 3. Tungsten in U.S.G.S. standards
(Chan and Riley, 1967)

Rock Type	Code number	W (p.p.m.)	Mo/W
Dunite	DTS-1	0.2	6.5
Peridotite	PCC-1	0.2	1
Basalt	BCR-1	0.7	4.1
Andesite	AGV-1	1.1	4.2
Granodiorite	GSP-1	0.5	5.2
Granite	G-2	0.4	4.8

These data do not show such an obvious gradual increase of tungsten in ultramafic to felsic rocks, parallel to the silica increase, as mentioned by Vinogradov et al (1958). Moreover the results of Chan and Riley (1967) are in general lower than those of Vinogradov et al. (1958). They are even below the lower limit of the range of tungsten abundances given by those authors (Vinogradov et al., 1958). Anyhow one should bear in mind that Vinogradov et al. (1958) used an average of at least eight analysed rocks for each group (ultramafic etc.), whereas Chan and Riley analysed only six samples, belonging to the four groups of rocks, and this without giving any conclusion about a certain trend of tungsten or so. Due to the small number of rocks analysed by Chan and Riley (1967) it does not make much sense to go into more detail about the Mo/W ratios as given by Vinogradov et al. (1958) and as calculated from the data of Chan and Riley (1967), although comparison shows a contradiction.

To conclude it should be mentioned that the method developed by Chan and Riley (1967) was adopted for use in the investigation of rock samples collected in the Salmo area in Southeast British Columbia, which can be considered as a tungsten-rich area. Difficulties, however, with the analytical procedure made it impossible to carry out this project as will shortly be explained.

CHAPTER II

PRELIMINARY ORIENTATION TESTS

Besides a few investigations with a mass spectrometer and, of course, neutron activation analysis, most analyses of silicate rocks for tungsten were done either with emission spectrography or colorimetry, after a pre-enrichment procedure.

Since the equipment was available for both spectrographic and colorimetric analysis a few orientation tests were carried out to find out the sensitivity that could be obtained.

Spectrographic determination

Orientation tests were carried out on synthetic samples with varying, but known, amounts of tungsten. Since no silicate rock samples had been analysed no wet chemical pre-enrichment procedure could be done either. A granite, however, was spiked with WO_3 in such a way that it contained, besides its original unknown amount of tungsten, 10,000 p.p.m. W. This enriched granite was then diluted several times with graphite to give samples with the following decreasing amounts of tungsten: 10,000 p.p.m., 5,000 p.p.m., 1,000 p.p.m., 100 p.p.m., 10 p.p.m. and 1 p.p.m.

The conditions under which the electrodes were burned were as follows: argon-oxygen, no filter, 1 screen, 7 amps, the electrode was 6.35 mm. deep and 2.44 mm. in diameter, 4 mm. gap between the electrodes. A I-N plate was used. The burning lasted three minutes.

The wavelength range of interest was 2400-5000Å. The most suitable lines are given in Table 4 together with the most strongly interfering lines.

Table 4. Suitable tungsten lines with possible interfering lines

(After Ahrens and Taylor, 1961)

Tungsten lines			Possible interference lines		
Wavelength	Element	Relative Intensity	Wavelength	Element	Relative Intensity
4008.753	W I	45	4008.928	Ti I	80
4294.614	W I	50	4294.128	Fe I	700
4302.108	W I	60	4302.192	Fe I	50
			(4301.934	Ti II	25)

The W-line 4008.753 seems to be the best line. Moreover the lines suggested here agree with W-lines suggested in recent literature (Taylor and Ahrens, 1950; Vinogradov et al., 1958).

Although the sensitivity of I-N plates shows a sharp decrease above 4500Å, within the range of interest they are almost as sensitive as the normally used 103-F plates.

The results were rather poor. At W 4008.753 tungsten could be measured at the 1000 p.p.m. level but not below. The least interference was noticed here. At W 4294.614 and W 4302.108 strong interference was noticed at the 5000 p.p.m. level. Both W-lines were very faintly visible at the 1000 p.p.m. level but not below.

The sensitivity is far below the sensitivity mentioned by Vinogradov et al (1958). Indeed, according to Kaufman and Derderian (1949, <u>in</u> Vinogradov et al., 1958) the sensitivity of the spectrographic determination of tungsten never exceeds 5 p.p.m. Moreover according to several Russian authors (Sergeev, 1947; Nedler, 1955; Shipitsin, 1950; Rusanov and Khitrov, 1957, <u>in</u> Vinogradov et al., 1958) the sensitivity in most cases is even less than about 10 to 100 p.p.m. It is true that most of their samples were ore samples, i.e. tungsten was present as a mineral and where a mineral is arced tungsten is fairly volatile due to the formation of WO_3, which, according to Ahrens and Taylor (1950) sublimes quite easily.

In the present work a granite matrix was enriched with WO_3, hence, because of the reasons given above, a better sensitivity might be expected than the one obtained. The reasons for this lower sensitivity are not known, but maybe some compounds or elements present in a silicate rock which are not present in tungsten ore might decrease the sensitivity.

To obtain an idea about the behaviour of tungsten as WO_3 and also to eliminate the influence of interfering elements experiments were carried out on three types of samples, i.e.:

- mixture of WO_3 and graphite
- mixture of WO_3-enriched granite and graphite
- mixture of WO_3 and NaCl.

The samples were made up in such a way that they each contained 5000 p.p.m. tungsten, since in previous experiments samples with 1000 p.p.m. did not give satisfactory results. From each sample two exposures were taken, i.e. one stationary exposure with seven steps and one moving exposure, in which the plate is racked every thirty seconds during three minutes, resulting in a spectrum containing six steps in chronological order.

The burning conditions remained almost the same, so only the changed conditions will be mentioned, i.e. the amperage was increased to 9 amps, burnings were done with and without argon-oxygen and a III-F plate was used.

The following conclusions were drawn from these experiments:

i. W 4008.753 remains the best line for investigation;

ii. use of the Stallwood jet (argon-oxygen) is recommended, since it gives a better line to background ratio;

iii. the tungsten intensity increases towards the end of the burning in the case of the WO_3 graphite mixture, while in the case of the WO_3-enriched granite the burning is more irregular.

iv. NaCl depresses strongly the volatilization of tungsten.

More time could have been spent to establish a reliable spectrographic method. Mainly because of the very low sensitivity however and also because of the increase of the tungsten intensity towards the end of the burning, which may result into an incomplete burn, further orientation tests were not carried out. The low sensitivity obtained with spectrography as mentioned in more recent literature (Špačková, 1965; Ivanova, 1966, _in_ Fleischer, 1968) was also a reason for abandoning spectrographical analysis.

Colorimetric determination

Orientation tests were carried out to try out the procedure developed by Jeffery (1959) for the routine examination for tungsten in a large number of rock samples.

The method itself is as follows: a rock sample (0.5g.) is fused with Na_2CO_3 in a platinum crucible. After leaching, iron-oxides etc. are removed by filtration. The filtrate is then acidified with H_2SO_4 to within a pH range of 0.5-2.0. Toluene-3:4-dithiol is added and the solution stands for one hour at 97-100°C. The precipitated Mo and W complexes are then extracted into petroleum ether. The absorbancy is measured at 630 mμ (Mo) and 680 mμ (W).

The wavelengths given (Allan and Hamilton, 1952) are 630 mμ for the W complex and 680 mμ for the Mo complex, and it is presumed that the wavelengths were inadvertently interchanged in Jeffery's article (1956). In the present work the absorbancy peak of tungsten was found to be in agreement with Allan and Hamilton (1952).

Neither the preliminary separation of Mo and W with α-benzoinoxime to separate both elements from interfering elements, nor the removal of silica as described in a previous method (Jeffery, 1956) were applied in this routine method.

Using this routine method Mo is partially precipitated and extracted (Jeffery, 1959), hence a correction must be applied in the same way as for the partial extraction of W with complete extraction of Mo (Jeffery, 1957). To apply this correction for Mo the absorbancy of the solution, which contains the complexes of both Mo and W (provided that Beer's Law is valid for the solution used and also that there is no interaction between the two complexes), is measured at the two wavelengths corresponding to the absorption maxima of the Mo and W complexes.

The absorbancies are additive and since absorbancy A, measured at a certain wavelength for a solution with one compound, it is expressed by the following equation:

$$A_\lambda = (\log\frac{I_o}{I})_\lambda = kcl$$

I_o = intensity of the incident light beam

I = intensity of the transmitted light beam

k = absorptivity or extinction coefficient (a constant depending on temperature, wavelength of light, etc.)

c = concentration of the component species

l = length of the light path.

hence the absorbancy for a solution with two compounds is given by:

$$A_{\lambda} = (k_1c_1 + k_2c_2)l$$

In a simultaneous determination of two elements, here Mo and W, the following measurements are carried out:

$$A_{630} = (k_1c_1 + k_2c_2)l$$

$$A_{680} = (k_1'c_1 + k_2'c_2)l$$

The constant absorptivities k_1, k_1', k_2 and k_2', where $k_1 \neq k_1'$ and $k_2 \neq k_2'$, are obtained by determination at wavelengths 630mμ and 680mμ in separate experiments, using only one substance; for example c_1 is a known amount of the Mo complex or c_2 is a known amount of the W complex. Hence a system of two linear equations with two unknowns is obtained.

According to Jeffery (1957), rearranging the equations when c_1 gives the Mo concentration and c_2 the W concentration, the ratio k_1/k_1' is obtained. This ratio is needed, since the constants k_1 and k_1' cannot be determined experimentally with known amounts of a standard Mo solution, as will be the case for the constants k_2 and k_2'.

$$A_{630} - k_2c_2l = k_1c_1l$$

$$A_{680} - k_2'c_2l = k_1'c_1l$$

hence

$$\frac{k_1}{k_1'} = \frac{A_{630} - k_2c_2l}{A_{680} - k_2'c_2l}$$

Applying this procedure for tungsten-free molybdenum solutions the ratio k_1/k_1' is determined without any knowledge of the proportion of molybdenum that has been extracted (Jeffery, 1957). From this ratio and the constands k_2, k_2' and l, the tungsten content of any sample can be determined.

The advantage of this method is that both Mo and W can be determined without separating them and this is a rather interesting feature because of the close relationship between the two elements. Since however the W- and Mo-dithiolates are not formed under the same conditions, i.e. the formation of the Mo complex is not complete in the pH range, within which the W complex is completely formed, the extraction is somewhat complicated.

For a simultaneous determination of both Mo and W in silicate rocks the ratio Mo/W or W/Mo should not exceed about 1 to 12 (Jeffery, 1956). This is not likely to happen in normal silicate rocks, but it would be a possibility for some of the rocks and minerals from Salmo, B.C., since the area of sampling is W-enriched.

In general the application of the methods proposed by Jeffery (1956, 1957, 1959) is rather complicated and somewhat controversial. In one method (Jeffery, 1956) silica must be removed with HF, after fusion of the rock sample with NaOH and $NaNO_3$, to prevent loss of Mo and W by precipitation with silica: in the routine method (Jeffery, 1959) silica removal is, however, not recommended.

The use of a short easy routine method is tempting especially when the more precise method proposed by the same author (Jeffery, 1956; 1959) is very tedious and time consuming.

Shortly after starting the application of this "routine method", the more recent method proposed by Chan and Riley (1967) was encountered. In this method the separation of Mo and W was said to be complete, silica was removed with HF, and the method, established under the control of a radioactive tracer, seemed to be less tedious and time consuming. These were the major reasons for abandoning the method proposed by Jeffery.

CHAPTER III

PHOTOMETRIC DETERMINATION OF TUNGSTEN
(METHOD OF CHAN AND RILEY)

Every time an investigation on tungsten geochemistry is published a new analytical method is proposed. Most of those methods are concerned with ores and/or alloys. Very few, however, deal with investigations at the p.p.m. level. A strange coincidence, or maybe not so strange at all, is the fact that no proposed method seems to have been used a second time.

The very recently developed spectrophotometric method of Chan and Riley (1967) seemed to be very sensitive and reliable because of the control carried out on several steps with W^{185} as a tracer. Indeed in the case of tungsten a reliable control is both necessary and difficult. The impression of trustworthiness was an argument in favour of adopting this method.

Description of the method

The following description of the analysis of sediments and silicate rocks is taken verbatim from Chan and Riley (1967, p.110-111):

"Weight out ca. 2g. of finely ground sample into a platinum basin. Add 8 ml. of 60% perchloric acid and 30 ml. of hydrofluoric acid. Cover the basin and heat overnight on a water bath. On the following morning remove the cover and allow the bulk of the liquid to evaporate. Continue the evaporation almost to dryness under an infrared heater. After cooling, add 4 ml. of perchloric acid, stir with a platinum rod and again evaporate almost to dryness. Repeat the fuming with a further 4 ml. of perchloric acid in order to remove all traces of fluoride. Add 2 ml. of perchloric acid and 40 ml. of water and heat the basin on the water bath until dissolution of the solids is complete.

Transfer the solution to a 500-ml. Erlenmeyer flask and dilute to ca. 250 ml. with water. Adjust to ca. pH 2 by cautious addition of 4 N ammonium hydroxide. Add 2 ml. of ethanol and 4 ml. of 0.5 N potassium permanganate solution. After allowing the solution to stand overnight, separate the precipitated hydrous manganese dioxide by centrifugation. Wash the precipitate with water and dissolve it in ca. 20 ml. of a saturated solution of sulphur dioxide in 0.05 N hydrochloric acid. Heat the solution to expel sulphur dioxide, dilute to ca. 50 ml. and pass it through a 10 x 1.2 cm. column of Zeo-karb 225. Elute tungsten along with the molybdenum and vanadium present in the sample using 100 ml. of 0.3% hydrogen peroxide. Continue the analysis as described for sea water.

Plate the eluate in a platinum basin and evaporate to 2-3 ml. Destroy the last traces of hydrogen peroxide by addition of a few drops of sulphur dioxide solution. Quantitatively transfer the solution to a 50-ml. separating funnel using not more than

10 ml. of water. Add 5 ml. of concentrated hydrochloric acid, 5 ml. of 2% (w/v) citric acid and 5 ml. of dithiol reagent and mix well. After 10 min. extract the green molybdenum complex with two 10-ml. aliquots of n-butyl acetate. Discard these extracts unless it is desired to determine molybdenum, in which case they should be combined, diluted to 25 ml. and the absorbance measured at 670 nm. in a 4-cm. cell.

Transfer the aqueous layer to a 50 ml. silica beaker, add 5 ml. of concentrated nitric acid and evaporate slowly. When the majority of the organic matter has been destroyed, add 2-3 ml. of 60% perchloric acid and heat on a hot plate until dense white fumes are evolved. Take up in 10 ml. of water, add a slight excess of ammonium hydroxide and boil off any excess ammonia. Add 5 ml. of 1 M hydrochloric acid, 1 ml. of 10% (w/v) hydroxylamine hydrochloride and 5 ml. of dithiol reagent. Warm to 80-90° on the water bath for 20 min. Cool to room temperature and then transfer the solution to a separating funnel. Extract the tungsten-dithiol complex with 5 ml. of butyl acetate and measure the absorption of the extract in a 4-cm. cell at 630 nm.

Carry out a reagent blank in the same manner but omitting the sample. Evaluate the results from photometric calibration runs made using 1 and 2 μg. of tungsten, multiplying the results by 1.05 to make allowance for the 95% recovery obtained in the separation process...".

Discussion of the method

Application of this method of Chan and Riley led to many difficulties, finally giving random results as shown in Table 5. This table shows the results of analyses of two batches of reference rocks and standard solutions in comparison with values obtained elsewhere (Chan and Riley, 1967; Atkins and Smales, 1960). In most cases a loss of tungsten was found.

Table 5. Results of analysis of reference rocks and standard solutions compared to values obtained by other authors

Standard solution (ppm) or standard rock	Values of present work	Values of other authors
0.6	0.3	-
0.6	>2.5	-
1.0	0.3	-
1.0	0.5	-
PCC-1	0.1	0.2*
DTS-1	>1.9	0.2*
W-1	>1.0	0.4**
GSP-1	0.2	0.5*
GSP-1	0.5	0.5*
G-2	≥0	0.4*

* Chan and Riley (1967)

** Atkins and Smales (1960)

The several steps where tungsten is likely to be lost - directly or indirectly - will be dealt with in this section. The different steps will be considered in their chronological order and labelled for convenience with a letter followed by a short description.

A. Attack with HF and $HClO_4$

This step, in which the finely ground sample was attacked with HF and $HClO_4$ in a teflon crucible (instead of a platinum one) mainly to eliminate silicon as the gas SiF_4, may contribute to a loss of tungsten due to a possible formation of WF_6. Indeed, this W compound is a gas with m.p. 2.5°C and b.p. 17.5°C. The formation of WF_6 depends on many factors like pH, form in which W occurs in the rock samples, e.g. as tungstates of Mn, Fe or Ca, as tungstenite (WS_2) or as W^{6+} substituting other elements like Nb^{5+}, Ta^{5+}, etc. In this situation the behaviour of W is rather complex.

Strong arguments, however, exist against a loss of tungsten as WF_6 with compounds like WO_4^{2-} or WO_3 as a point of departure, since W should be reduced first before WF_6 can be formed (Chrétien and Freundlich, 1963). This is not very likely to happen because of the presence of $HClO_4$, which is a very strong acid and oxidizing agent.

Moreover, equilibria involving compounds like WF_6 and water are displaced far to the oxide side according to the following reaction:

$$WF_6 + H_2O \rightleftharpoons WO_3 + HF$$

According to Ivanova (1966) and Krauskopf (1964) in a study about the behaviour of W in magmatogenic processes, only completely unreasonable concentrations of halogen acids are required for the presence of WF_6 in a gas phase. Whereas this might be the case here, the presence of $HClO_4$ however should not be forgotten.

A tungsten loss does not seem very likely in this early step for the reasons given above, although this could be stated with certainty only after establishing a reliable control for example with a tracer.

B. Drying

To dry the content of the crucibles infrared lamps were used, whilst the temperature was measured in a teflon crucible containing only $HClO_4$ (60%). The temperature indicated about 140-150°C.

The drying process itself is not likely to cause any direct tungsten loss, although indirectly this step might be of influence afterwards, due to the fact that not all traces of fluoride might have been removed. This may result in the formation of stable fluoro-compounds not taking part in later reactions (Chrétien and Freundlich, 1963).

The specification "almost to dryness" (Chan and Riley, 1967, p.110), although baking is not allowed (Chan and Riley, 1966), can cover a wide range even for a single rock sample or group of rock samples like granites for example, not to mention the broad difference between drying the residue of a felsic or ultramafic rock sample.

An optimum in each case must exist, but since a tungsten loss in this step is not very likely, i.e. a tracer **cannot** be used, it is difficult to find out when the optimal conditions are reached.

C. Dissolution

After the drying process the solids are treated with 2 ml. of $HClO_4$ and 40 ml. of water and heated on the water bath supposedly until complete dissolution of the solids. With the exception of the standard solutions, the dissolution of the solids is never complete. In almost every case there remains a very fine precipitate, which even after hours on the water bath cannot be dissolved.

Although the amount of this precipitate is very small (maybe 1 mg.) it is not known how far it might cause a loss of W, if it really does. Anyhow the qualitative spectrographic analysis of such precipitates revealed the occurrence of the following elements: Si, Al, Mg, Ca, Ba, Sr, Fe, Ti and Mn.

Since the precipitation of one element might provoke the co-precipitation at the same time of some other elements (this will be considered more in detail below) one should be aware that a possible loss of W might occur in this step, although it is not very likely with so small amounts of precipitate.

Certainty could only be obtained by checking this step with a radioactive tracer.

D. Co-precipitation with hydrous manganese dioxide

In this step it is not very likely that there will be some tungsten loss, so that a further consideration in detail of this step may not be very relevant. The fact, however, that a slight precipitate was found in step C above, and that an even more voluminous precipitate occurs in step E below when dissolving the hydrous manganese dioxide precipitate, makes it worthwhile to consider this step in some detail.

For the co-precipitation of tungsten several hydroxides can be used, for example those of Al, Ti, Fe and Mn. This however does not mean that the results with each of those hydroxides are ideal. Fe and Mn hydroxides co-precipitate W within a certain pH range, giving a recovery yield of 97-98% for Mn hydroxide and an even higher yield for Fe hydroxide, though Mn hydroxide is more selective in its action (Tanaka, 1958; Ishibashi et al., 1962, in Chan and Riley, 1967; Chan and Riley, 1967).

The Ti- and Al-hydroxides are of much less interest due to their low recovery yield. In other words Ti-hydroxide is not very interesting as a co-precipitant for the reasons given above, but it might interfere and cause a loss of W because it precipitates instead of going into solution. It is more appropriate to reconsider this situation of step E when the co-precipitate is going to be dissolved.

The only real difficulty occurring during the co-precipitation with MnO_2 is the time factor. Especially the intermediate rock samples need more than 12 hours (standing overnight) to settle down completely. In some cases 48 hours were not sufficient for a complete precipitation. The question remains open whether there might be a loss of W by separation through centrifuging the bulky coagulated mass from the liquid before it settled down completely. The only possible control is checking liquid and precipitate with a radioactive tracer.

Besides a possible W loss (not proved), an anticipated separation causes difficulties for two reasons: first, it is more difficult to get a clear solution by centrifuging on top of the precipitate and second, the centrifugation time needed is much longer.

E. Dissolution of the co-precipitate in 0.05N HCl saturated with SO_2

The main idea of this step is the complete dissolution of the hydrous manganese dioxide precipitate, which solution will be run through an ion-exchange column (see below). The MnO_2 precipitate usually dissolves completely in the HCl-SO_2 solution. To expel the SO_2 the solution is heated and becomes colourless. At the same time, however, a white (somewhat milky) colloidal suspension forms (Maxwell, 1968). Further heating does not seem to reduce the amount of the colloid, instead the size of the particles become much finer (fine white powder). When not heated the solution also becomes colourless and forms a white colloidal suspension, although more slowly, i.e. after an hour or so.

Tests to find out whether the white suspension might be some colloidal sulphur or not were negative (Maxwell, 1968). The white suspension was then filtered off, ashed and investigated qualitatively with the spectrograph. This control confirmed the presence of Ti, Fe, Mn, Zr and Cr, but also Si, Al, Mg, Ca, Ba and Sr, which is not surprising since the precipitate occurring in step C was never filtered off. It should be emphasized that the Ti, Fe and Mn spectra are much stronger than in the first spectrographical investigation, as mentioned in step C. Neither Mo nor W lines could be detected, which is not surprising if one takes into account the low sensitivity of the spectrograph and also the possible interference of Fe.

The presence now of Ti in the residue may cause problems throughout the further procedure. As is explained in step C, when considering the co-precipitation with $MnO_2.H_2O$, Ti-hydroxide is an agent for co-precipitating tungsten. It is rather unsuccessful however since according to Chan and Riley (1967) only 68% of tungsten is co-precipitated at pH 3.8 using 30 mg. Ti^{3+}.

The fact that Zr and Cr are found in this white precipitate might be a warning that W can also be absorbed by this Ti compound, and although maybe not such high amounts of Ti are available as mentioned above, the amounts seem to be large enough to be considered for a possible W loss.

For this reason the white residue was not filtered off. It should be added, in cases where the white residue seemed to be more abundant, i.e. more in intermediate rock samples than in felsic ones (see also Table 6), this residue settles on the glass wall and cannot be removed, which causes another possibility for tungsten loss.

Table 6. Weight percent of TiO_2 in igneous rocks and the earth's crust in relation to the SiO_2 content

	Earth's Crust (1)	Ultramafic* (2)	Mafic* (2)	Intermediate*	Felsic*
SiO_2	55.2	43.8	48.4	54.6	68.9
TiO_2	1.6	1.7	1.8	1.5	0.5

* Igneous rocks, Nockolds (1954)
1 Poldervaart (1955)
2 With exclusion of those rocks containing nepheline

Ti probably occurs in this residue as an oxyhydrate. If really a Ti-oxyhydrate is formed it becomes obvious that any tungsten loss preferentially will occur here because orthotitanic acid ($TiO_2.2H_2O$) is a voluminous hydrogel and very absorbant. By boiling the dihydrate forms the more granular, less absorbant metatitanic acid ($TiO_2.H_2O$) (Chrétien and Freundlich, 1963; Scheffer, 1961).

The Ti hydrogel is not filtered off, because it might contain W, so that in fact a colloidal solution is run through the ion-exchange columns.

Again the only way to control any tungsten loss is with the already mentioned radioactive tracer.

F. Ion-exchange

Chan and Riley (1967), after carrying out several experiments with anion-exchangers, disregarded this type of ion-exchange, due to unsatisfactory recoveries of W. Indeed, in the most favourable case, i.e. elution with 1 N HCl containing 88 g. of ascorbic acid/litre the recoveries of W were very good, up to 98% and more, as long as not less than 100 μg. is present. Working at the microgram level, however, ca. 1 μg. is tenaciously retained by the anion-exchanger.

For this reason Chan and Riley (1967) carried out experiments with the cation-exchange resin Zeo-Karb 225 (8% D.V.B., 52-100 mesh). They state that W could be satisfactorily eluted with ca. 120 ml. of 0.3% H_2O_2, although they do not mention the amounts of W worked with nor recovery yields. Both authors refer in this situation to Ryabchikov and Bukhtiarov (1960) and Strelow (1963), who were investigating at mg. levels.

In the present work Dowex 50W (8% D.V.B., 52-100 mesh), another strongly acidic cation-exchange resin with nuclear sulphonic acid as the active group, has been used.

In a strongly acid cation-exchange resin the following reaction normally occurs (Korkisch, 1969), e.g. for a monovalent cation M^+:

$$R_sSO_3^-H^+ + M^+ \rightleftharpoons R_sSO_3^-M^+ + H^+$$

where R_s = resin matrix.

The selectivity of an ion, W^{6+} in this particular case, that is the extent to which one ion is absorbed in preference to another, is very important and depends on factors like charge, size, polarizability, hydration, i.e. nature of the exchanging ions, and nature of the functional group and the degree of cross-linking in the resin.

The selectivity decreases with an increasing concentration (feed solution) and temperature.

For practical purposes it is important to know (Korkisch, 1969):

$$\text{weight distribution} = Kd = \frac{c_1}{c_2}, \text{ where}$$

c_1 = weight of metal ion adsorbed on 1 g. of the dry resin,

c_2 = weight of metal ion which remains in 1 ml. of solution after equilibrium has been reached.

It is also necessary to know the separation factor α, for the element of interest (a) relative to other elements (e.g. b), determined under identical experimental conditions, where

$$\alpha = \frac{Kd_a}{Kd_b} \qquad (\alpha \text{ must not be } \neq 1)$$

Since no use is made of an anion-exchanger for the separation of W^{6+} for reasons given above, the attention will be given to the cation-exchange. According to Korkisch (1969) W is predominantly present as an anion in dilute acid, with the consequence that its adsorption on cation-exchange resin is relatively low. Although it seems paradoxical to separate an anion using a cation-exchange resin, several authors applied this separation method (Strelow, 1963; Ryabchikov and Bukhtiarov, 1959; Fritz and Dahmer, 1965; Korkisch, 1969).

In HCl solutions, with acidities ranging from 0.2 N to 4 N the Kd of Mo decreases from 11 to 0.3 (Strelow, 1960, in Korkisch, 1969). No data are given for W, although according to Figure 1 the Kd of W never becomes greater than 1 for a range of 2 N to 12 N HCl. In other words, in the case of W there seems to be almost no adsorption with HCl solutions with normality less than 2. In 10 N $HClO_4$ the Kd of Mo is about 10^4 and about 10^3 for W under the same conditions (Nelson, Murase and Kraus, 1964, in Diamond and Whitney, 1966).

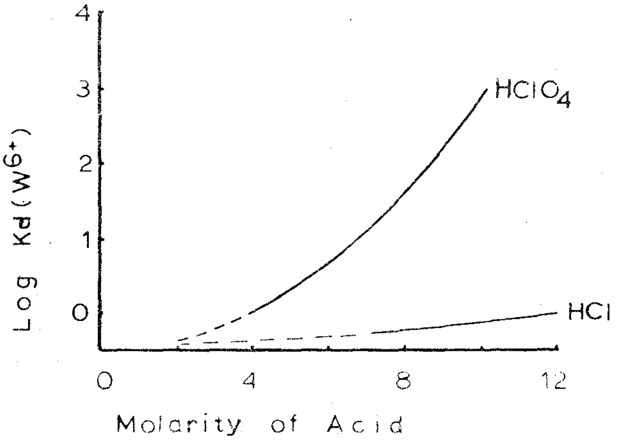


Figure 1. Log Kd of W from $HClO_4$ and HCl solutions by a cation exchange resin

(after Nelson, Murase and Kraus, 1964; Diamond and Whitney, 1966).

The present work was carried out at much lower acidities. At mineral acid concentrations lower than 6 N (and greater than 9 N) hydrolytic species of tungsten are formed, which may cause the precipitation of tungstic acid (Nelson, Murase and Kraus, 1964, <u>in</u> Korkisch, 1969).

Although various experiments have been carried out with H_2O_2 as an eluent for Mo^{6+}, W^{6+}, Nb^{5+} and Ta^{5+} from cation-exchange columns, only a very small number of separations, carried out under considerably varying conditions and most of them on the mg. level, have been reported (Fritz and Dahmer, 1965).

According to Strelow (1963) for example, Nb^{5+}, V^{5+} and Mo^{6+} (presumably also W^{6+}) are only very weakly or not at all adsorbed. These elements can be eluted with 0.5 N H_2SO_4 containing 1% H_2O_2, passing directly through the column. Concerning W this author mentions that W^{6+} behaves like Nb^{5+} and that it can be separated from Ti, although its tendency to hydrolyze does not make this separation always reliable. Experiments were done on the mg. level.

Ryabchikov and Bukhtiarov (1959), also working on an mg. level, used cation-exchange to separate Ti from W. In order to avoid adsorption they worked with a solution of pH 5, added H_2O_2 and used a fast flow rate (3 to 4 ml. per minute). All the W passed into the filtrate.

Fritz and Dahmer (1965) made synthetic sample mixtures of (~0.25 mmole) Mo, and 0.5 mmole of W, Nb and Ta with an approximately equal amount of a second metal ion. As evidence for complete elution of W, with 80 to 90 ml. of 1% H_2O_2 in 0.25M H_2SO_4, they ashed some of the resin and analyzed it for W with emission-spectrometry. No W was detected in the resin.

H_2O_2 seems to be the only valuable eluent for W as becomes obvious from the few reports on the elution of W, although it may be mixed with some acid, generally H_2SO_4. Chan and Riley (1967) used 0.3% H_2O_2 without anything else. Following their procedure there was always gas formation during the elution for any rock type analyzed. This gas formation, however, has never been observed when eluting a blank or standard sample. Strelow (1963) mentions that V if not present in the five valent state leads to serious bubble formation and consequently distortion of the resin-bed which reduces the yield of the elution. Again a tracer might help here to detect a certain W loss, if occurring.

The low or even non-adsorbability of W on a cation-exchanger makes the use of a cation-exchange resin somehow versatile. In other words W can be separated by elution or with the effluent. The main factor to control this versatility is the pH. Very little however is known concerning the behaviour of W so that too often an analogy has to be made with Mo, assuming a more or less similar behaviour for W. As is the case for Mo, W presumably will be held in solution in acidic media of pH 1-2. There is a danger for important W losses either by precipitation as tungstic acid on the resin, which is favoured by increasing pH, or by disappearing with the effluent. The way to be sure is, again, by using a radioactive tracer. Besides this certainty it could help also in obtaining optima flow rates for adsorption and elution and optima pH since these have not been mentioned by Chan and Riley (1967).

G. Tungsten extraction

Whereas the Mo extraction stage did not cause any difficulties this cannot be said for the W extraction. A minor problem was the elimination of HNO_3. Chan and Riley (1967 p.110) specify this step "until dense white fumes are evolved". White fumes, however, occur when there is still some HNO_3 left and when the evaporation goes too far the solution becomes brown giving afterwards a cloudy extract with n-butyl-acetate.

Of more importance is the fact that the oversaturated solution, according to Chan and Riley (1967), must be taken up in 10 ml. of water. This amount is sufficient to precede the neutralisation with NH_4OH (with less water the reaction is a violent one), but is however not enough for dissolving the salts at room temperature and should, therefore, be some 6 times more. For this reason, in the present work the W-dithiolate solution was brought over into a separation funnel and HCl of pH ≤ 1 was added. This was to prevent the formation of unsoluble species except the W complex and also to keep the pH of the solution within a certain range. If the HCl-containing solution is not clear, i.e. if still some little crystals are left, then these crystals partly go over into the n-butyl-acetate making it cloudy and therefore unreadable, since only W-dithiolate is soluble in this solvent.

To obtain a 100% extraction of W-dithiolate with an organic solvent, here n-butyl-acetate, the acid normality must be kept within a certain range, as is shown in Table 7.

Table 7. Effect of acidity on extractability of tungsten-dithiolate

(after Chan and Riley, 1967, p.108)

Acid normality before addition of dithiol	0.04	0.12	0.20	0.28	0.36	0.80	1.60	2.40	3.50
Tungsten extracted in %	86	100	100	100	100	90	62	36	13

In the present work the pH of the solution was kept as much as possible within the range 0.8-1.1, corresponding with a HCl normality of about 0.1-0.3.

It is not very likely that W is lost with the extraction of Mo, nor that a W extraction of less than 100% is obtained. Complete certainty however could only be obtained with the aid of a tracer, checking the extraction solvent containing the Mo or W complex, as well as the solutions from which both Mo and W were extracted.

Since several attempts now have been made on rocks both with and without known amounts of W, giving only random results, it was decided to carry out analyses several times on one and the same rock type to find out the optima conditions of the several steps of the procedure discussed above. A granodiorite (VA-1)

Table 8. Tungsten content in a granodiorite (B.C.) under varying conditions

	D	E	F	G	H	I	J	K	L
Ion-exchange:									
Adsorption time (50 ml. solution)	330'	320'	305'	350'	320'	168'	174'	135'	135'
Elution time (100 ml. solution)	115'	105'	90'	36'	59'	52'	36'	77'	45'
Absorbancy:									
Molybdenum	0.045	0.070	0.086	0.038	0.053	0.062	0.031	0.057	0.042
Tungsten	⩾0	⩾0	⩾0	0.024	0.003	0.008	0.006	0.002	0.002
W in p.p.m.	-	-	-	0.59	0.06	0.19	0.15	0.05	0.07

from British Columbia (Nelson area) was taken since no standard rock samples were available in large enough amounts. The main idea was to change (e.g. for the first step) one condition in a few samples and then carry on to the second step, etc. This would have been ideal, if each step could have been controlled. This was not possible because of the lack of a good control and because of the limited time. The results are shown in Table 8. Only those steps are given which seem to be particularly critical.

The sample G gives the most reasonable results, because all the other samples give W amounts too low for intermediate rocks, according to Vinogradov et al. (1958). This is not to imply however that the results for G are correct. The conditions established for sample G were used for a batch of standard solutions and standard rocks, as well as sample VA-1, for which the final results are given in Table 9.

Out of these results it becomes obvious that the values obtained are far too low. Only in one case (VA-1) the same result has been obtained, and then only in one of the two samples analyzed.

The only improvement is that the new results are less random now in the sense that no very high values were obtained (see Table 5). To what extent, however, this may be called a positive result is doubtful, since it is now certain that somewhere, somehow, tungsten is definitely lost.

Table 9. Results obtained for standard rocks, standard solutions and VA-1 compared to the results of other authors (in p.p.m.)

Standard solution or rock	Amount of W found in present work	Values given by other authors
1	⩾0	-
2	1.4	-
2	⩾0	-
2	0.1	-
DTS-1	0.1	0.2*
W-1	0.2	0.4**
W-1	0.3	0.4**
AGV-1	0.2	1.1*
GSP-1	⩾0	0.5*
G-2	0.2	0.4*
VA-1	0.1	0.6***
VA-1	0.6	0.6***

* Chan and Riley (1967)

** Atkins and Smales (1960)

*** Present work (Table 8)

Calibration of the working curve

According to Sandell (1959) and Chan and Riley (1967) Beer's Law is obeyed for this W complex solution, which means that absorbancy plotted versus concentration gives a straight line. The law is expressed by the following equation:

$$A\lambda = (\log \frac{I_o}{I})\lambda = kcl \quad \text{(see Chapter II)}$$

The absorbancy (optical density) of known amounts of W-dithiolate dissolved in n-butyl-acetate was plotted versus wavelength. The spectral absorbancy curve shows for each sample a maximum at 630 mμ, so measurements were done at this wavelength.

For the construction of the working curve solutions with known amounts of W are, according to Sandell (1959) supposed to be analyzed in the same way as a normal rock sample. This was done but resulted in scattered data, for reasons explained above. Therefore the standard solutions were treated as if Mo just had been extracted, i.e. starting from the point where the aqueous layer with W is brought over into a silica beaker (see method Chan and Riley, 1967). Samples with known amounts of W within the range 0.2 to 2.4 p.p.m. at intervals of 0.2 p.p.m. were analyzed. The working curve also obtained (Figure 2) has the following characteristics:

Equation of the standard curve (regression line y on x):

$$y = 46.228\,x - 0.0098$$

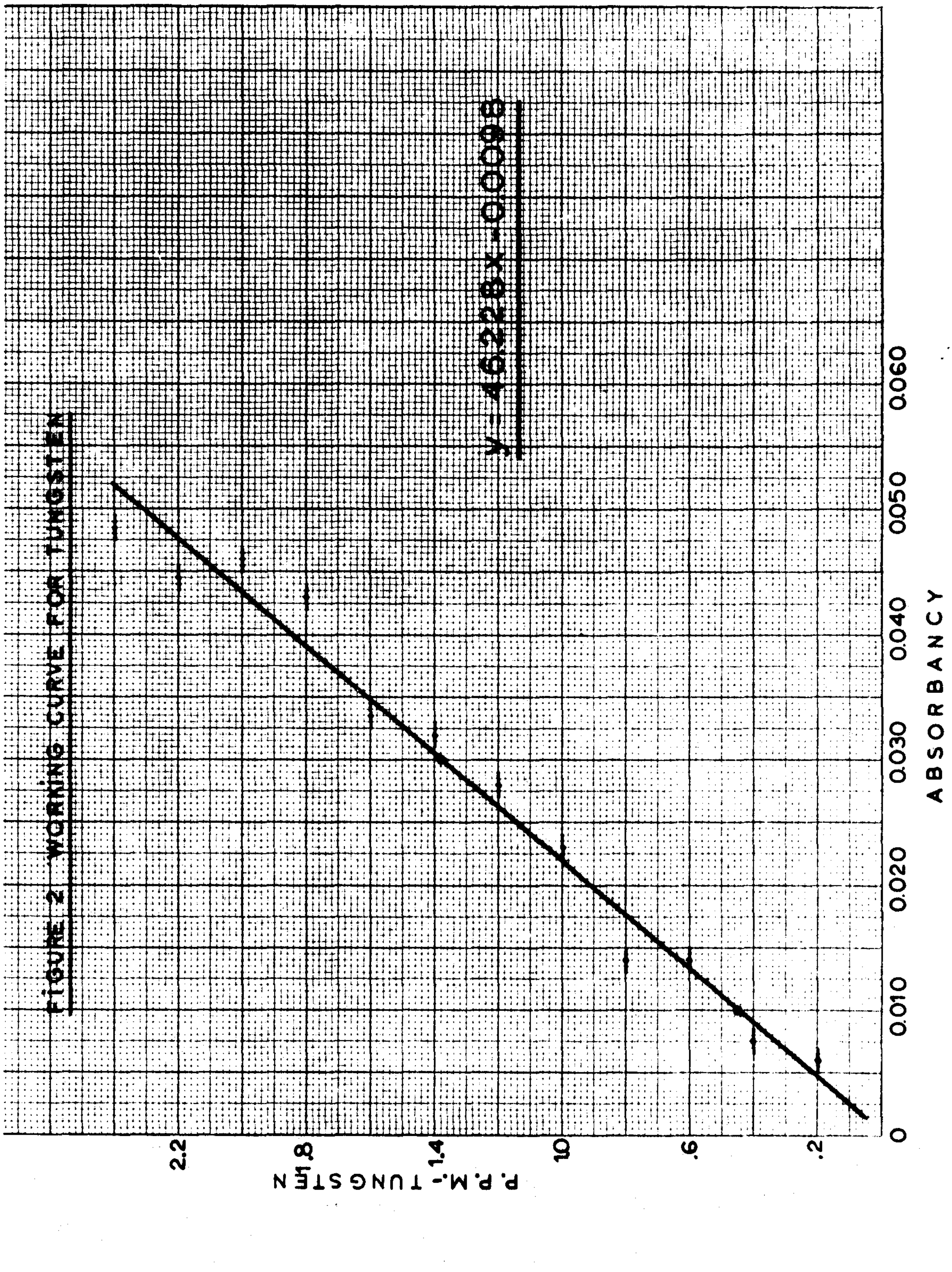


FIGURE 2 WORKING CURVE FOR TUNGSTEN

y = amount in p.p.m.

x = absorbancy

standard deviation:

$s_y = 0.12$

$s_m = 2.228$

$s_b = 0.078$

coefficient of determination:

$r^2 = 0.9728$

coefficient of correlation:

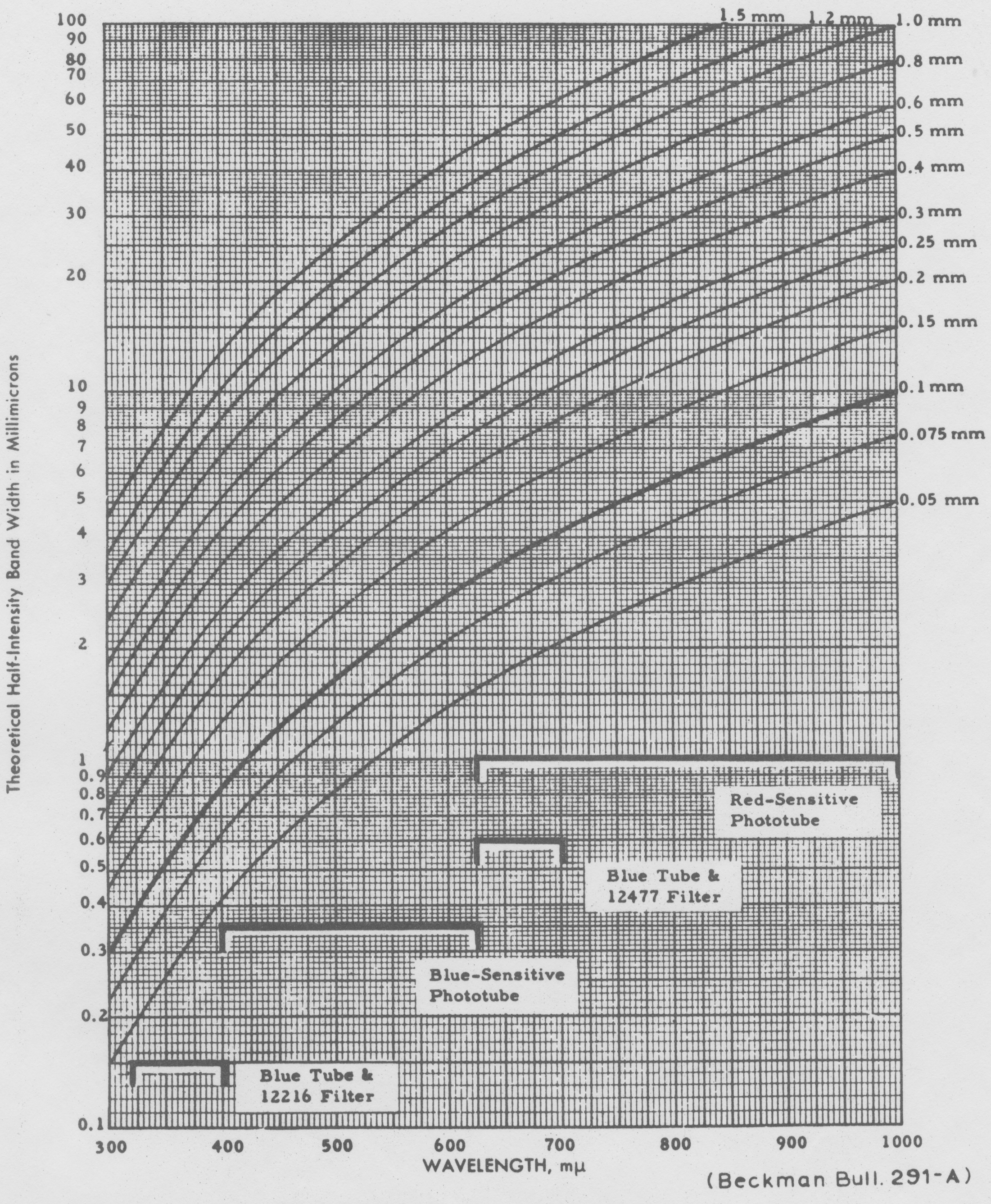
$r = +0.986$

The correlation coefficient is very close to 1, which means that there is almost no unexplained variation. Thus it may be accepted that Beer's Law is obeyed here, since the absorbancy is directly proportional to the concentration.

The absorbancy of rock samples and of standard solutions was measured at 630 mμ with a Beckman Model B spectrophotometer, using a slit width of 0.34 mm. The slit adjustment control varies the width of the entrance and exit slits simultaneously and is used primarily to zero the photometer with the blank in the light path. For maximum resolution narrow slit widths are recommended although the slit setting should not be less than 0.1 mm.

According to the Beckman manual the blue sensitive phototube is suggested for the wavelength range below 675 mμ whereas the red sensitive one should be used above 675 mμ.

According to Figure 3, the upper limit for the blue sensitive phototube without filter is 625 mμ which at the same time is



(Beckman Bull. 291-A)

Figure 3. Half-Intensity Band Width Curve

the lower limit for the red sensitive one, also used without filter. Hence at the wavelength of interest measurements could be done with either the red or the blue sensitive phototube. In the latter case a filter should be used.

All the measurements in the present work were done with the red sensitive phototube (the needle was more stable). The disadvantage of the red phototube is that for any given slit width a wider band of wavelengths will pass than when using the blue one.

With a slit width of 0.34 mm. at 630 mμ a theoretical half-intensity band width of 11 mμ is obtained. Each wavelength contributes at least half as much energy as does the wavelength with the greatest energy, i.e. here 630 mμ . The half-intensity band width is equal to the half-spectral band width. The slitwidth of the exit should be adjusted to a minimum since an increase in the half-intensity width causes broader absorption bands, hence a decrease in absorption maxima.

It should be mentioned that Chan and Riley extracted tungsten with 5 ml. of n-butyl-acetate, which seemed to be enough to fill an adsorption cell with a path length of 4 cm. In the present work, however, cells with a path length of 1 cm. (≃5 ml.) and 5 cm. (≃15 ml.) were available, and those with a path length of 5 cm. were preferred. The 1 cm. cell has a path length which is too short, but the 5 cm. cell necessitates a dilution, resulting in an amount five times greater than that used by Chan and Riley (1967). The only advantage of this dilution, which was necessary due to the large content of the 5 cm. cell, is the fact that at least two extractions could be made.

CHAPTER IV

CONCLUSIONS

After completing the work described in the preceding chapters, it was found that Johansen and Steinnes (1970) had very recently determined tungsten in standard rocks by neutron activation using HF for the decomposition of the samples and anion-exchange separation. The following elements were determined:

Co, Cu, Fe, Ga, Zn and W.

A better than 97% recovery and a reproducibility of the order of 1% were found for all 5 elements except W. 30-40% of this element was eluted with Cu. The rest was found on the column after the elution, maybe due to hydrolysis. The authors used a reactivation step, since part of the W amount remained on the resin, for the determination of the chemical yield, and thereafter determined W in the same fraction as Cu.

Their results disagree considerably (up to the order of 1 magnitude) with those of Chan and Riley (1967) as shown in Table 10.

Compared with the data of Chan and Riley (1967) the data of the present work are in general lower without any trend. The same can be said for a comparison with the data of Johansen and Steinnes (1970) with the exception of the granite G-2.

Johansen and Steinnes mention that their results for

Table 10. A comparison between the data of Chan and Riley (1967), Johansen and Steinnes (1970) and the present work (in p.p.m.)

Standard rock	Spectrophotometric 1	Spectrophotometric 2	Neutron-activation 3
DTS-1	0.2	0.1	-
W-1	-	0.3	0.38
W-1	-	0.2	0.38
AGV-1	1.1	0.2	0.45
GSP-1	0.5	$\geqslant$0.0	0.12
G-2	0.4	0.2	0.04

1 Chan and Riley (1967)

2 present work

3 Johansen and Steinnes (1970)

tungsten are not as precise as for the other elements investigated, mainly because of the low W content in the samples. Where they mention a precision of 1.3% for Fe and about 3% for Co, Cu, Ga and Zn, they give no figures for W. Nevertheless it should be emphasized that their results for W-1 are still in reasonable agreement with previous literature data (Table 11), whereas Chan and Riley did not analyze W-1.

There appear to be two suitable methods for analysis of W in silicate rocks, leaving open the question which one is the better:

1. colorimetry - when using this method it is quite obvious

Table 11. Tungsten content in W-1 by Neutron Activation

Tungsten content in W-1 (in p.p.m.)	Various authors
0.46	Ahrens and Fleischer (1960)
0.40	Atkins and Smales (1960)
0.46	Amiruddin and Ehmann(1961)
0.58 (av. of 5)	Hamaguchi and others (1962)
0.45	Fleischer and Stevens (1962)
0.38	Johansen and Steinnes (1970)

that the optima for the different steps should be determined, as well as the steps where a loss of tungsten can occur. This can be done with a radioactive tracer like W^{185}, which has a half life of 75 days. The work already done by previous authors should be repeated almost completely, retaining only the several steps of the procedure.

2. neutron activation - the use of this method is more restricted, due to the need of more sophisticated equipment, not to mention reactor facilities. Assuming those facilities exist, it seems to be more desirable to use neutron activation instead of colorimetry. W has five stable isotopes which can complicate investigations. Since these show only a slight percentage difference in mass, they are not expected to show an appreciable separation in natural processes. Indeed, no separation has been reported yet (Krauskopf, 1970).

Table 12. Nuclear data for tungsten

(Compilation by R. L. Heath, 1963)

Target Isotope	% natural abundance	Isotopic activation cross section (barns)	Product on neutron activation	Radiation & energy	Half-life
W^{180}	0.14	<20	W^{181}	E.C. γ 0.1525, 0.1361	130d
W^{182}	26.41	0.5	W^{183m}	I.T.	5.5s
		20	W^{183}	stable	
W^{183}	14.40	11	W^{184}	stable	
W^{184}	30.64	-	W^{185m}	I.T. γ 0.135, 0.175	1.62m
		2.1	W^{185}	β^- 0.432	75.80d
W^{186}	28.41	40	W^{187}	β^- 0.63, 1.315, 0.34 >10γ's - 0.68, etc.	24h

A few nuclear data on tungsten are given in Table 12, from which it becomes obvious that the reaction $W^{186}(n,\gamma)W^{187}$ seems to be very suitable for neutron activation analysis.

Although neutron activation analysis is a time consuming procedure, as is the colorimetric method, it has the advantage of greater sensitivity and less need of quantitative recovery.

REFERENCES

AHRENS, L.H. and TAYLOR, S.R., 1961, Spectrochemical Analysis. A treatise on the d-c arc analysis of geological and related materials. Addison-Wesley, London.

ALLEN, S.H. and HAMILTON, M.B., 1952, The estimation of molybdenum and tungsten by dithiol. Anal. Chim. Acta, 7, 483-493.

AMIRUDDIN, A. and EHMANN, W.D., 1962, Tungsten abundances in meteoritic and terrestrial materials. Geochim. Cosmochim. Acta, 26, 1011-1022.

BECKMAN INSTRUMENTS, Instruction Manual, Bull. 291-A, p.6.

CHAN, K.M. and RILEY, J.P., 1966, The determination of molybdenum in natural waters, silicates and biological materials. Anal. Chim. Acta, 36, 220-229.

_________ and __________, 1967, Determination of tungsten in silicates and natural waters. Anal. Chim. Acta, 39, 103-113.

_________ and __________, 1967, Determinations of vanadium, molybdenum and tungsten in the new series of U.S.G.S. analyzed samples. Chem. Geol., 2, 171-172.

CHRÉTIEN, A. and FREUNDLICH, W., 1963, Titane, nouveau traité de chimie minérale. Dir. P. Pascal, IX, Masson & Cie, Paris.

___________ and ______________, 1963, Tungstène, nouveau traité de chimie minérale. Dir. P. Pascal, XIV, Masson & Cie, Paris.

DELAHAY, P., 1957, Instrumental Analysis. MacMillan, N.Y.

DIAMOND, R.M. and WHITNEY, D.C., 1966, Resin selectivity in aqueous solutions. In Ion-Exchange (ed. J.A. Marinsky), I, 341-2, Marcel Dekker Inc., N.Y.

DOROKHINE, I., BOGATCHEVA, E., DROUGININE, A., SOBOLEVSKY, V. and GORBOUNOV, E., 1967, Gisements de minéraux utiles et leur prospection. Editions "Ecole Supérieur", Moscow.

FLEISCHER, M., 1965, Summary of new data on rock samples G-1 and W-1, 1962-1965. Geochim. Cosmochim. Acta, 29, 1263-1283.

_____________, 1968, U. S. Geological Survey standards. I. Additional data on rocks G-1 and W-1, 1965-1967. Geochim. Cosmochim. Acta, 33, 65-79.

FLANAGAN, F.J., 1969, U. S. Geological Survey standards. II. First compilation of data for the new U.S.G.S. rocks. Geochim. Cosmochim. Acta, 33, 81-120.

FRITZ, J.S. and DAHMER, L.H., 1965, Cation exchange separation of molybdenum, tungsten, niobium and tantalum from other metal ions. Anal. Chem., 37, 10, 1272-1274.

HAMAGUCHI, H., KURODA, R., SHIMIZU, T., TSUKAHARA, I. and YAMAMOTO, R., 1962, Values for trace elements in G-1 and W-1 with neutron activation analysis. Part II. Mo, Sn, Ta, W. Geochim. Cosmochim. Acta, 26, 503-505.

HEATH, R.L., 1963, Table of the isotopes (compilation). Handbook of Chemistry and Physics, ed. 1968-1969.

IVANOVA, G.F., 1966, Thermodynamic evaluation of the possibility of tungsten transport as halogen compounds. Geochem. Int., 3, 5, 964-973.

IVANOVA, G.F., 1969, Conditions of concentration of tungsten during gneisenization. Geochem. Int., 6, 1, 12-21.

JEFFERY, P.G., 1956, The simultaneous photometric determination of molybdenum and tungsten in silicate rocks. Analyst, 81, 104-109.

_____________, 1957, Photometric determination of molybdenum in tungsten ores. Analyst, 82, 558-563.

_____________, 1959, The geochemistry of tungsten, with special reference to the rocks of the Uganda Protectorate. Geochim. Cosmochim. Acta, 16, 278-295.

JOHANSEN, O. and STEINNES, E., 1970, Determination of Co, Cu, Fe, Ga, W and Zn in rocks by neutron activation and anion-exchange separation. Talanta, 17, 5, 407-414.

KORKISCH, J.K., 1969, Modern methods for the separation of rarer metal ions. Pergamon Press, Toronto.

KRAUSKOPF, K.K., 1970, Tungsten (Wolfram). Handbook of Geochemistry II-2. Ed. K.H. Wedepohl. Springer Verlag.

LYAKHOVICH, V.V. and BALANOVA, T.T., 1969, Mean contents of W, Mo, Sn, Ta, Nb and Zn in sphene and ilmenite from granites. Geochem. Int., 6, 2, 281-287.

MASON, B., 1966, Principles of Geochemistry. Wiley, N.Y.

MAXWELL, J.A., 1969, Rock and Mineral Analysis, Interscience, N.Y.

RYABCHIKOV, D.I. and BUKHTIAROV, V.E., 1960, Separation of titanium from tungsten by ion-exchange chromatography. Translated from Zhurnal Anal. Khimii, 15, 2, 242.

SANDELL, E.B., 1959, Colorimetric Determination of Traces of Metals. Interscience, N.Y.

SCHEFFER, E.R., 1961, Titanium, treatise on analytical chemistry. Eds. I.M. Kolthoff and P.J. Elving, Part II, 5, 1-60. Interscience, N.Y.

ŠPAČKOVÁ, A., 1965, Spektrochemische Bestimmung von Molybdän und Wolfram in Gesteinen. Czechoslov. Chem. Commun., 30, 1255-1259.

ŠTEMPROK, M. and ŠULCEK, Z., 1969, Geochemical profile through an ore-bearing lithium granite. Econ. Geol., 64, 392-404.

STRELOW, F.W.E., 1963, Separation of titanium from rare earths, beryllium, niobium, iron, aluminum, thorium, magnesium, manganese and other elements by cation-exchange chromatography. Anal. Chem., 35, 9, 1279-1282.

TANAKA, M., 1958, Méthode de précipitation à pH constant des oxydes hydratés: principe et applications en microanalyse du chrome et du molybdène. Microchim. Acta, 2, 204-211.

VINOGRADOV, A.P., VAINSHTEIN, E.E. and PAVLENKO, L.I., 1958, Tungsten and molybdenum in igneous rocks (as related to the geochemistry of tungsten). Geochemistry, No. 5, 497-509.