SPECTROGRAPHIC DETERMINATION OF RHENIUM IN MOLYBDENITE WITH THE D.C. ARC

by

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INTRODUCTION

The emission spectroscope has been known as one of the most versatile analytical tools available to the scientist. Spectroscopic methods have been especially useful, both qualitatively and quantitatively, for the determination of metal elements present in samples of all types of materials. The simplicity, rapidity, accuracy of identification, and precision of spectrographic emission analysis have become widely recognized during the past three decades.

Rhenium is one of the extremely rare elements. It is geologically associated with molybdenum, and in molybdenite the concentration of rhenium is sometimes sufficient for spectrochemical analysis. In molybdenite, rhenium concentration may reach a maximum of 0.1 per cent. At 0.01 per cent rhenium can be detected by use of rhenium emission lines at 3464.0 and 3460.5 A. However, the presence of constituents other than the one under investigation may affect line intensities, especially for larger quantities of the extraneous elements (greater than 1 per cent). It was considered, therefore, that the concentrations of molybdenum, iron and copper in molybdenite could cause considerable effect on the line intensity of rhenium. This research attempted to separate rhenium from those interfering elements and apply the d.c. arc as a spectrographic source for the determination of rhenium in molybdenite. Concentration of rhenium also could be accomplished during the separation of rhenium in the molybdenite samples.

SURVEY OF THE LITERATURE

The presence of molybdenum, iron and copper in molybdenite may cause considerable effect on the line intensity of rhenium, so it is desirable to separate rhenium from interfering elements by some chemical means previous to spectrographic analysis.

In the past, a variety of chemical separations of rhenium from molybdenum have been developed on a micro as well as macro scale. Among these may be listed the distillation method of Geilmann and Weibke (11), which utilized the technique of passing a stream of moist hydrogen chloride diluted with CO_2 through a hot concentrated H_2SO_4 solution of the perrhenate, followed by a gravimetric determination of the rhenium which collected in the distillate. In another method advanced by these authors (12) the molybdenum was separated by precipitation from nearly neutral solutions with 8-hydroxyquinoline. Both methods work satisfactorily for the ranges in which they were intended, but when applied to the problem of separating five g. lots of molybdic anhydride from 0.1 mg. or less of rhenium are not at all satisfactory.

Much the same may be said of the methods of Kronman and his students (21), as well as of the work of Mikhailova, Pevsner, and Archipova (26) who used a combination of the distillation method with the 8-hydroxyquinoline method to effect the determination. The rhenium was generally determined by a nitron acetate precipitation. In all these variations on fundamental methods, none of the authors obtained the high degree of separation needed to make a simple and effective method for the determination of rhenium in a molybdenite mineral. Thus, the best that Mikhailova, Pevsner, and Archipova were able to do was to determine mg. amounts of rhenium with an accuracy of 0.4 to 0.3 per cent in the presence of not more than twice that amount of molybdenum.

In an early paper by Hurd (17), a method was described whereby the molybdenum was extracted from solutions containing rhenium by first treating with ethyl xanthate, followed by chloroform extraction of the molybdenum complex thus formed. The rhenium was then determined by reaction with stannous chloride and potassium thiocyanate (10). Although the method was satisfactory for qualitative work, it could not be used for quantitative determinations without additional refinements.

Willard and Smith (32) have developed a method whereby the perrhenate may be precipitated from solutions with tetraphenyl arsonium chloride. From the work of these authors, it is apparent that the molybdate does not interfere greatly, but unfortunately, it is not possible to precipitate the minute amounts of rhenium which are usually present in the molybdenites.

Hoffmann and Lundell (16) have used a differential reduction with mercury to effect the required separation. Under certain conditions only the molybdate is reduced and this may be extracted with ether after treatment with a thiocyanate. Separations of as much as 10 mg. of molybdenum from 0.001 mg. of rhenium have been claimed. This method would be satisfactory if it were not so detailed and if the order of separation were higher.

Hurd and Hiskey (18) developed a method which was capable of determining as little as one part of rhenium in twenty million of pyrolusite. In this method the rhenium was isolated by an extraction of the thiocyanate complex, followed by a modified distillation procedure. Since there was scarcely any molybdenum in these minerals, the difficulty of separation was not particularly great, and thus the method, although somewhat cumbersome, was satisfactory.

A completely satisfactory method for the quantitative determination of rhenium in molybdenite minerals had never been developed until 1940, because

of a combination of several analytical difficulties. Chemical similarity of rhenium and molybdenum makes clear-cut separations somewhat difficult. Secondly, though molybdenites contain the highest natural concentrations of rhenium that have been found, these concentrations are usually of the order of 0.001 to 0.0001 per cent. In addition, no colorimetric reaction for the determination of rhenium had been developed in which molybdenum does not interfere. Consequently, it is necessary to eliminate molybdenum before any rhenium estimation can be made, and it is in this operation that most of the difficulties arise. However, Hiskey and Meloche (15) developed a method for the quantitative determination of five microgram quantities of rhenium in the presence of millionfold excess of molybdenum which combines a modified distillation and modified colorimetric technique. It was applied to the analysis of 28 molybdenite samples.

More recently, ion-exchange chromatographic methods have been studied for the separation of rhenium from molybdenum (1, 2, 5, 8, 14, 25, 30). Fisher and Meloche (9) had successfully separated mixtures of perrhenate and molybdate ions by use of ion-exchange resins. Their procedure consisted of adsorbing both molybdate and perrhenate on Amberlite IRA-400, followed by removal of the molybdate selectively with 2.5N NaOH solution, and finally elution of the retained perrhenate with 7N HCl. The removal of molybdate by NaOH and perrhenate by HCl was time consuming because of the large volume of eluting agents required. An improvement had been made by Meloche and Preuss (25) in the procedure for the separation of perrhenate from molybdate ions using Amberlite IRA-400 (ClO_4^-) wherein the volume of eluting agents and the time required were reduced considerable. $K_2C_2O_4$ was recommended for the separation and elution of the molybdate ion and $HClO_4$ for the subsequent elution of the perrhenate ion.

EXPERIMENTAL

Description of Apparatus

The spectrograph used in this research was a Bausch and Lomb large Littrow instrument with interchangeable quartz and glass optics. Quartz optics were used for this research. The instrument has a wavelength range of 2100 to 8000 Angstrom units and a linear dispersion of 105 Angstrom units per millimeter at a wavelength of 2150 Angstrom units and 6 Angstrom units at a wavelength of 3350 Angstrom units. The quartz prism is of the Littrow type, 57 millimeters high with a reflection coating of evaporated aluminum. The combination collimation and focusing lens has a focal length of 1827 millimeters and is provided with two stops for reducing aperture.

The illuminating system consisted of the electrode holders, a spherical condensing lens, and a rotary sector disk. Line intensities were obtained by means of an Allied Research Laboratories-Dietert Densitometer.

The samples were excited with a direct current generator capable of producing a potential of 150 volts, the current depending on the resistance of the circuit. A ballast resistor was placed in series with the generator to stabilize the current. Currents of approximately 12 amperes were used.

Determination of Exposure

In order to properly compare the amount of rhenium in the sample with the standard, it is necessary that the sample be completely vaporized. The rate of vaporization will depend on the material on the electrodes and the temperature of the arc. By making a moving plate spectrum of a sample of the spectrographic standard containing the highest amount of rhenium, it was found that all of the rhenium was vaporized in approximately 20 seconds.

To account for variations in the arc the samples were, therefore, excited for 30 seconds.

Since the rhenium line used falls very near the region of the cyanogen bands, it is difficult to reduce plate background without seriously affecting line intensities. It is possible, however, by careful use of a rotating sector to reduce background to such a value that no correction is required. The sector was set at ¼ open and rotated at a speed greatly exceeding 50 interruptions per exposure for all exposures. If the number of interruptions for each exposure exceeds 50, Brode (6) has reported that the intermittancy effect is negligible.

Preparation of Electrodes

Spectrographic graphite electrodes purchased from the National Carbon Company were used in these analyses. They were prepared for use by cutting the 12 inch carbons into 5/4 inch lengths. The anode was prepared by drilling a well in one end of the electrode, four to six millimeters in depth with walls one millimeter thick. The cathode was shaped to a sharp point similar to a pencil.

The anode was prepared for the sample by filling the well with a solution of carbon tetrachloride saturated with carnauba wax. Following this the electrodes were dried in an air oven for 15 minutes at a temperature of 110°C.

Spectrographic Procedure

With a pipet, a 0.1 ml. aliquot of the standard or unknown solution was placed on the prepared electrodes. The electrodes with the solutions were dried in an air oven at 110°C for several hours, preferably overnight.

Eastman type spectrographic analysis No. 1 plates were selected as the most sensitive plates available. The samples were arced with a d.c. potential of 150 volts and a current of 12.5 amperes for a period of 30 seconds with the sector ½ open. The slit width was set at 50 mμ. A series of standards were run on each plate.

After exposure the plates were developed for five minutes at a temperature of 68°F in Eastman D-19 developer, then fixed, washed and dried. The line intensities were determined with the aid of an A.R.L.-Dietert densitometer. A slight background correction was necessary. The results were expressed in parts per million of rhenium on the basis of the molybdenite.

Preliminary Work

The rhenium line of wavelength 3460.5 A is probably most satisfactory for quantitative analysis. However, the rhenium occurring in molybdenite must be separated from the interfering elements and concentrated by some chemical means previous to spectrographic analysis. Table 1 shows a list of the possible interfering lines and their wavelengths.

Table 1. Possible interfering lines that appear in the region of the rhenium line located at 3460.5 A.

Element	Wavelength, A	Relative line intensity
Rhenium	3460.5	1000W
Chromium	3460.43	40
Cobalt	3461.18	100wn
Copper	3459.43	25
Iron	3459.92	80
Manganese	3460.33	60
Molybdenum	3460.78	25

In the paper by Meloche and Preuss (25), an ion-exchange separation of molybdenum and rhenium was recommended and the fusion method was used for the dissolution of rhenium containing ores. The following procedure was recommended. Pass the sample solution obtained after fusion through 5 g. of the perchlorate form of Amberlite IRA-400 in an ion-exchange column, at a rate of 10 to 20 ml. per minute. Rinse the column with 100 ml. of water at a rate of 1 to 2 ml. per minute. Then remove the adsorbed molybdenum with 300 ml. of 1 M $K_2C_2O_4$ solution at a rate of 2 ml. per minute. Rinse the column with 50 ml. of water to remove any excess of $C_2O_4^{=}$ ion. Then pass 200 ml. of 1 M $HClO_4$ through the column and dilute the effluent to exactly 250 ml., take a suitable aliquot and determine rhenium concentration using the method employing α-furildioxime.

In this laboratory, the ion-exchange separation method was tried by passing 25 ml. of 10^{-3} M/l $KReO_4$ solution through the column. Spectrographic analysis of the water washing solution, however, indicated the presence of rhenium. Therefore, the perrhenate ion was not completely adsorbed and after several trials this method for the separation of molybdenum and rhenium was abandoned.

Separation using the anion-exchange resin Dowex 1-X8, also were not satisfactory, although a variety of different experimental conditions were tried.

Preliminary studies then were made using principles of extraction suggested by the work of Peterson et al. (28) and Maeck et al. (23). After the samples of molybdenite had been placed in solution by acid treatment, followed by removal of iron, chromium etc., with NH_4OH, the rhenium was extracted with tetrabutyl ammonium bromide in NaOH solution. The extracting phase was 4-methyl-2-pentanone.

This procedure, checked by spectrographic methods, seemed to provide quantitative separation and extraction of rhenium from the major constituents of molybdenite and thus was the procedure selected for further study as the separation and concentration step in the analytical procedure.

Calibration Curve for Position Five

Since the spectrum length of the large Littrow spectrograph is about 80 centimeters, it is possible to photograph only a limited portion of it at a time. There are 10 different positions of the prism necessary to photograph the entire spectrum. Position five was selected to photograph the rhenium lines. Because the instrument may not be in the same adjustment as when it left the factory, and the focus and tilt prescribed by the manufacturer may not be the best for the region of the spectrum in which the rhenium line occurs, it was thought advisable to check the recommended values of focus and tilt. This was done by photographing a series of iron spectra with the tilt set at the recommended value and varying the focus a few divisions on each side of the given value. Examination of the plate after development showed the focus to be best at 107.5 for position five. Making a similar plate by setting the focus at 107.5 and varying the tilt, the tilt was found to be best at 242. These settings were used for all analyses in position five.

Because the dispersion of a prism is not linear, it was necessary to prepare a calibration curve for each position. To do this a millimeter scale was printed across the top of the plate and directly below this an iron spectrum. After development of the plate, the wavelengths of several iron lines were determined by comparison with a standard iron spectrum provided with the instrument by the manufacturer. After location of a few wavelengths in this manner, others were determined using the iron spectrum charts compiled

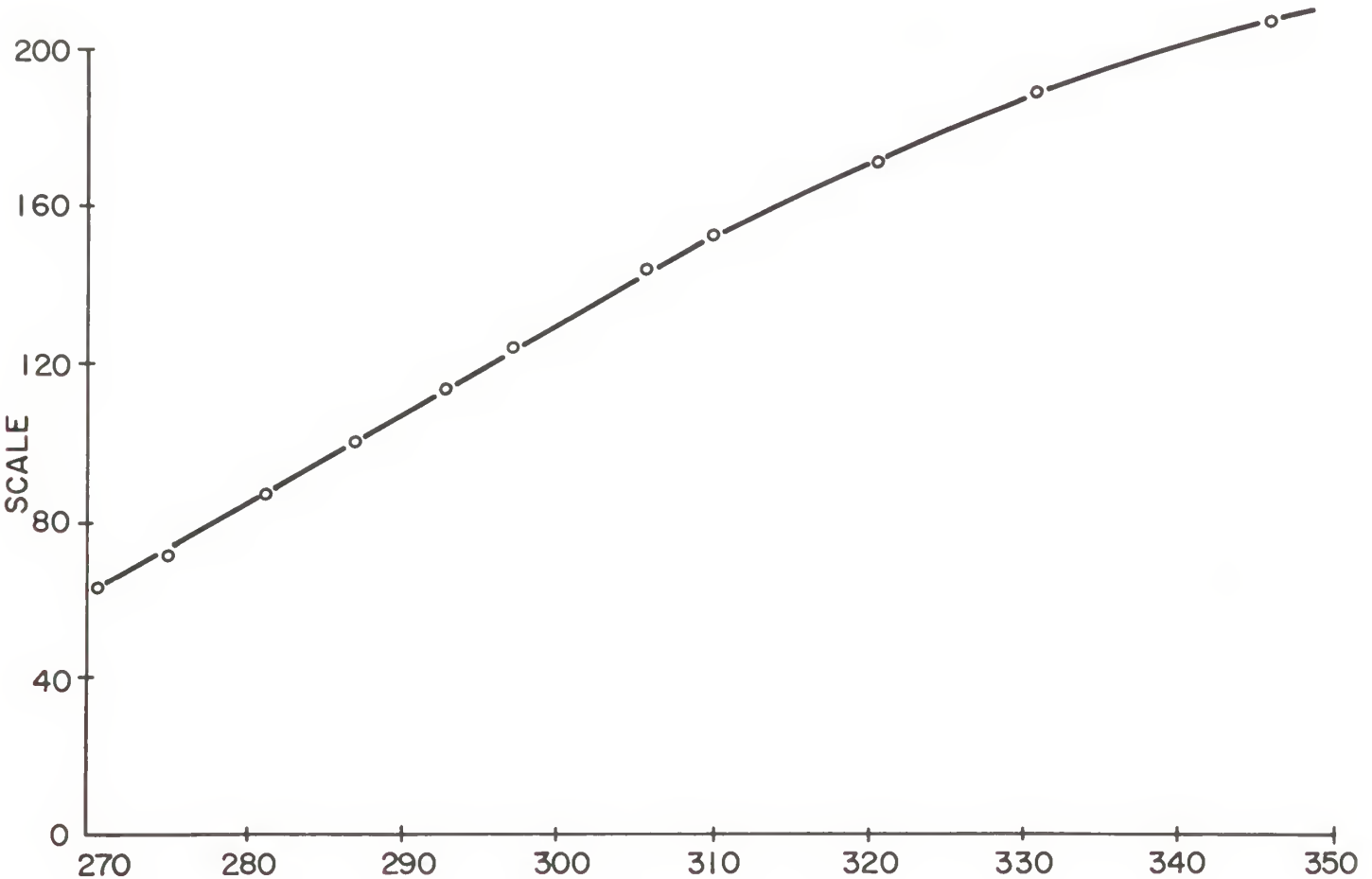

FIG. 1 DISPERSION CURVE

by Brode (6). The wavelengths thus determined were plotted against the scale readings to obtain the dispersion curve, Fig. 1.

Selection of Internal Standard

Gerlach and Schweitzer (13) were the first to report the use of an internal standard to compensate for variations likely to occur in the arc during the excitation of the sample. The internal standard may be one of the following two types: a weak line of a major constituent of samples; of a small, unvarying amount of an element added to each sample. Preparation of a series of standard samples with varying amounts of rhenium and a constant amount of a reference element, followed by observation of the intensity ratio between the reference element and the rhenium lines, provides the basis of a working curve.

The internal standard method assumes that variations in excitation conditions will affect the unknown and reference element in the same manner. Also, the difference in densities of the two lines is assumed to be proportional to the logarithm of the ratio of intensities of these lines in the source. The latter is true only for the straight line portion of the characteristic curve of the photographic emulsion in question.

In making a series of exposures for the same sample the line densities vary widely. This is especially true of an element which is highly volatile. The principle reason for this lies in the fact that it is impossible to control the many variables in the arc which will tend to change the rate of vaporization of the sample. The probability of exciting the vaporized atoms will then change with time. In order to account for these variations the internal standard should have the following characteristics:

1. The concentration of the internal standard in the analysis specimens is

negligibly low.

2. The internal standard and analysis lines have similar excitation potentials.
3. The rates at which internal standard and analysis element volatilize are very similar.
4. The internal standard line is free from self-absorption.
5. Analysis and internal standard lines are roughly the same wavelength, so as to reduce errors that might occur in the photographic measurement of radiant energy.
6. The internal standard is in a very high state of purity with respect to the element sought.
7. The internal standard is homogeneously mixed with the sample.
8. The ionization potential of the internal standard is similar to that of the analysis element.

It was desirable to select an internal standard element which possessed as many of the previously mentioned characteristics as possible. In practice, no element fulfills all of them, however, cobalt meets the majority of the requirements, so it was chosen for use as the internal standard in this analysis of molybdenite for rhenium. Both cobalt and rhenium have similar excitation potentials, being 4.00 and 3.57 volts respectively. Cobalt has a suitable spectral line near the 3460.5 A rhenium line, located at 3453.0 A. The boiling points, however, are quite different. The ionization potentials for rhenium and cobalt are 7.85 and 7.86 volts respectively. The remaining requirements are easily met in the establishment of experimental conditions.

SPECTROGRAPHIC ANALYSIS OF MOLYBDENITE USING THE RHENIUM LINE AT 3460.5 ANGSTROM UNITS

Preparation of the Standards

Standards were prepared by complexing the perrhenate ion with tetrabutyl ammonium bromide and extracting the complex into 4-methyl-2-pentanone for four times from a sodium hydroxide system (23). To 1 ml. of potassium perrhenate solution, 2 ml. tetrabutyl ammonium bromide solution (Eastman Kodak White Label), 2 ml. of sodium hydroxide and 5 ml. 4-methyl-2-pentanone (Eastman Kodak White Label), were added and mixed for five minutes. After centrifugation and separation of the two layers, the extractions of the aqueous layer were repeated three more times using 5 ml. quantities of pentanone and adding the extractants together. The extracts were then evaporated to dryness and treated twice with 2 ml. of concentrated nitric acid. After the solution was evaporated to dryness the second time, 1 ml. of 0.1 N hydrochloric acid solution was pipeted into the residue and 1 ml. of a 0.1 molar solution of $CoCl_2.2H_2O$ was added as the internal standard. A series of standards were made by using varying amounts of the standard rhenium solution and a constant amount of the internal standard, as shown in Table 2.

In order to form the working curve shown in Fig. 2, 0.1 ml. of the spectrographic standard was pipeted on each electrode. The electrodes were then dried in an air oven at 110°C for several hours. Cobaltous chloride hydrate used as the internal standard was checked spectrographically to show that rhenium was not present as an impurity.

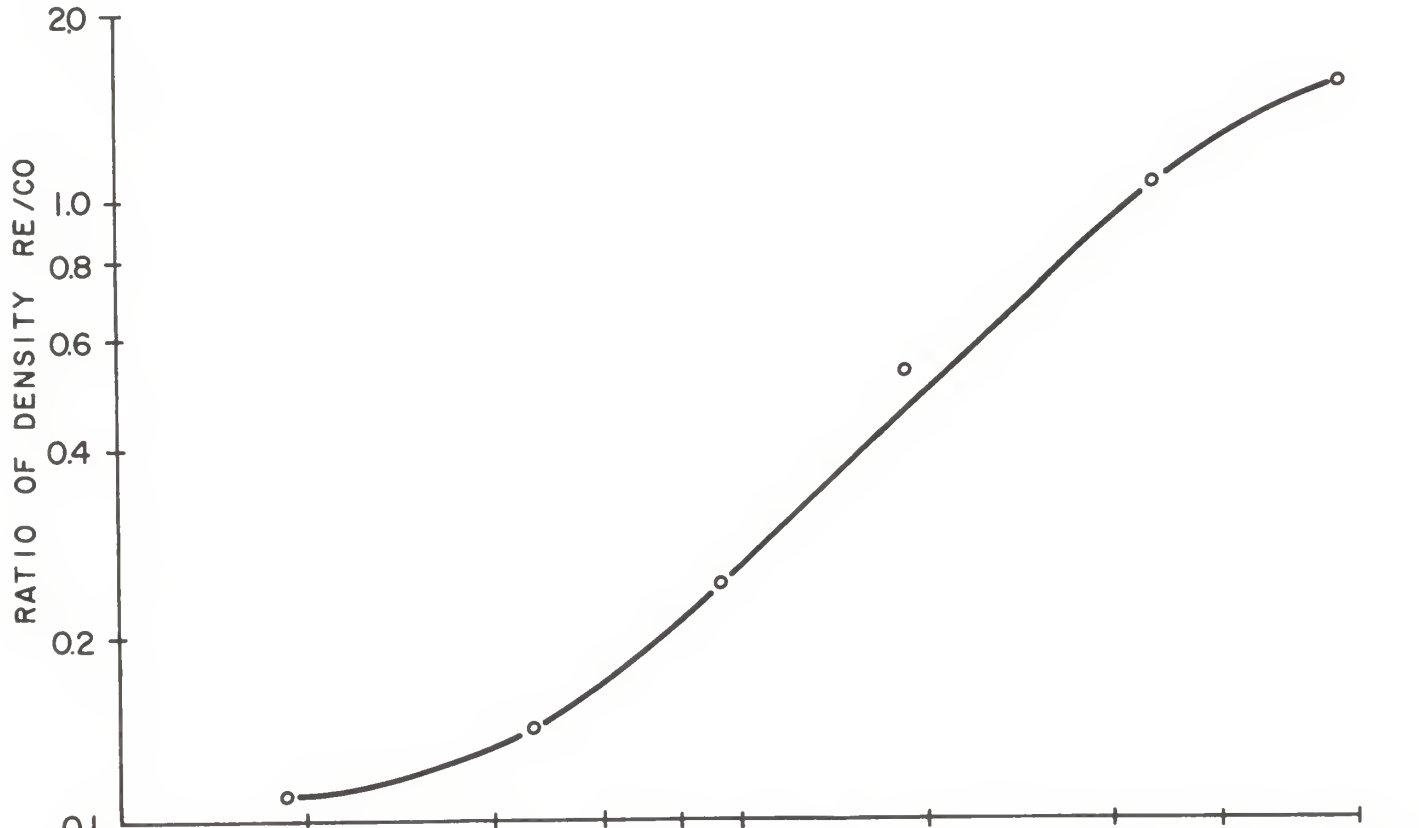

FIG. 2 WORKING CURVE FOR RHENIUM

Table 2. A series of spectrographic standards for use with the rhenium line at 3460.5 Angstrom units.

Standard No.	Internal standard solution, ml	Rhenium solution ml	Rhenium amount ppm
1	1.0	0.10	18.6
2	1.0	0.25	46.5
3	1.0	0.50	93.0
4	1.0	1.00	186.0
5	1.0	2.50	465.0
6	1.0	5.00	930.0

Preparation of the Sample Solution

A certain amount of molybdenite (0.4, 0.5 and 1.0 g. samples of molybdenite ore for the high, medium and low levels of rhenium respectively) was weighed, treated with 25 ml. of concentrated HNO_3 and heated to almost dryness. Following this, concentrated HCl was added to dissolve most of the white precipitate. The brownish residue that remained was removed by filtration. Then excess NH_4OH solution was added to the filtrate to remove iron, chromium, etc. as the hydroxide precipitate. The filtrate was evaporated to about 2 ml. and the rhenium extracted. This was done by adding 2 ml. of 0.1 M tetrabutyl ammonium bromide solution, 2 ml. of NaOH and 5 ml. 4-methyl-2-pentanone, and allowed to mix for five minutes.

After centrifugation and separation of the two layers, the extraction on the aqueous layer was repeated three more times using 5 ml. quantities of the pentanone, and adding the extracts together. The extracts were evaporated to dryness and the residue treated twice with 2 ml. of concentrated HNO_3 and

evaporated to dryness again. The residue thus obtained was dissolved in one ml. of 0.1 N HCl and one ml. of 0.1 M $CoCl_2.2H_2O$ internal standard was added. After the solution was mixed thoroughly, it was ready for the spectrographic electrodes.

Precision of Analysis

The precision of this method of analysis was determined by several analyses on the same sample. Averages were obtained and the deviations and probable errors were calculated. Tables 3, 4 and 5 present data which indicate the precision of the method in the analyses of three samples of molybdenite. The probable errors were calculated to be 2.71, 3.36, 4.33 per cent for high, medium, low levels of molybdenite respectively. These three samples averaged 815.8, 406.8, 84.4 ppm of rhenium for the high, medium, and low levels respectively when analyzed by the spectrographic technique and 950, 442, 90 ppm when analyzed colorimetrically.

Method of Standard Addition

In order to verify the results already obtained, the method of standard additions was used. A known amount of the standard solution was added to the sample solution. The final solution would include rhenium from both the standard and sample solutions. By subtraction of the known amount of rhenium added from the total, the rhenium contained in the sample could be obtained. Tables 6, 7 and 8 show results obtained by adding three different concentrations of potassium perrhenate solution to each sample; one of them contained more, one had about the same amount, and the other was less than the amount of rhenium which was in the sample. In this analysis, 0.2, 0.3 and 0.5 g. of sample ores were used for the high, medium and low levels of molybdenite respectively.

Table 3. Analyses of molybdenite (high level of rhenium) to show precision of the spectrographic method using the line at 3460.5 Angstrom units.

%T Re	%T Co	I_{Re}/I_{Co}	ppm/gram	D	D^2
40.6	27.1	0.692	725	90.8	8244.64
37.5	26.4	0.728	757	58.5	3457.44
36.0	27.6	0.795	842	26.2	686.44
30.7	24.6	0.830	875	59.2	3504.64
29.2	22.8	0.833	880	64.2	4121.64
Total			4079		20014.80
Average			815.8		

$$S = \text{Standard deviation} = \sqrt{\frac{\Sigma D^2}{n-1}} = \sqrt{\frac{20014.80}{4}} = 70.7$$

$$\text{Standard error} = S_X = \frac{S}{\sqrt{n}} = \frac{70.73}{\sqrt{5}} = 31.6$$

$$\text{Probable error} = S_x \cdot \frac{\sqrt{2}}{2} = (31.580)\,(0.7) = 22.1$$

$$\text{Per cent standard error} = \frac{31.580}{815.8} = 3.87\%$$

$$\text{Per cent probable error} = \frac{22.106}{815.8} = 2.71\%$$

Table 4. Analyses of molybdenite (medium level of rhenium) to show precision of the spectrographic method using the line at 3460.5 Angstrom units.

%T Re	%T Co	I_{Re}/I_{Co}	ppm/gram	D	D^2
56.2	28.1	0.453	354	52.8	2787.84
50.5	23.0	0.466	368	38.8	1505.44
49.8	26.9	0.532	422	15.2	231.04
46.1	24.2	0.544	434	27.2	739.84
41.4	21.3	0.569	456	49.2	2420.64
Total			2034		7684.80
Average			406.8		

S = Standard deviation = $\sqrt{\frac{\sum D^2}{n-1}} = \sqrt{\frac{7684.80}{4}} = 43.8$

Standard error = $S_X = \frac{S}{\sqrt{n}} = \frac{43.78}{\sqrt{5}} = 19.5$

Probable error = $S_X \cdot \frac{\sqrt{2}}{2} = (19.544)\ (0.7) = 13.7$

Per cent standard error = $\frac{19.544}{406.8} = 4.80\%$

Per cent probable error = $\frac{13.681}{406.8} = 3.36\%$

Table 5. Analyses of molybdenite (low level of rhenium) to show precision of the spectrographic method using the line at 3460.5 Angstrom units.

%T Re	%T Co	I_{Re}/I_{Co}	ppm/gram	D	D^2
76.1	22.4	0.182	67	17.4	302.76
72.6	22.0	0.214	81	3.4	11.56
69.2	20.7	0.232	87	2.6	6.76
71.3	23.6	0.233	88	3.6	12.96
72.7	29.5	0.260	99	14.6	213.16
Total			422		547.20
Average			84.4		

$$S = \text{Standard deviation} = \sqrt{\frac{\Sigma D^2}{n-1}} = \sqrt{\frac{547.20}{4}} = 11.7$$

$$\text{Standard error} = S_X = \frac{S}{\sqrt{n}} = \frac{11.69}{\sqrt{5}} = 5.22$$

$$\text{Probable error} = S_X \cdot \frac{\sqrt{2}}{2} = (5.218)\,(0.7) = 3.70$$

$$\text{Per cent standard error} = \frac{5.218}{84.4} = 6.18\%$$

$$\text{Per cent probable error} = \frac{3.653}{84.4} = 4.33\%$$

Selection of the Spectrographic Buffer

Photoelectric densitometry has greatly increased the precision of measurement of spectral line intensities because small variations in these intensities can be detected. Several factors contribute to these variations which affect analytical data. Among these is the effect of extraneous elements in the arc. This condition is due at least in part to the transport mechanism of ions across the arc. Transport phenomena in arc sources may be the result of an equilibrium between thermal diffusion of material from the region of the electrode and a migration of ions of the sample due to electrical forces. Langstroth and McRae (22) have investigated transport phenomena and reached the following conclusions:

1. Lines of different elements have, in general, different intensity distributions along their lengths.
2. The relative distributions depend on ionization potentials and masses of the elements, and on the ionization potentials of other atoms present in the discharge.
3. When easily ionized atoms are present in the discharge, the distribution of an element relative to that of a more easily ionized element of comparable mass falls off more sharply toward the unloaded electrode than it does when easily ionized atoms are absent.

The purpose of the spectrographic buffer is to minimize variations in the transport mechanism from spectrum to spectrum. Requisites of an acceptable buffer are that it does not emit a complicated spectrum of its own, and that it has a low ionization potential.

Since the majority of spectrographic work in this laboratory has been done using chloride salts, the use of lithium chloride as a buffer was

Table 6. Analyses of molybdenite (high level of rhenium) to show precision of the spectrographic standard addition method using the line at 3460.5 Angstrom units.

%T Re	%T Co	I_{Re}/I_{Co}	ppm obtained	ppm added	ppm/gram true	D	D^2
40.1	23.8	0.637	260	93	835*	59.1	3492.11
42.6	28.3	0.676	277	"	920	25.9	670.81
28.4	21.5	0.820	348	186	810	84.1	7072.81
31.2	26.7	0.880	375	"	945	50.9	2590.81
23.1	24.6	1.046	459	279	900	5.9	34.81
25.5	27.8	1.068	470	"	955	60.9	3708.81
Total					5365		17570.16
Average					894.1		

S = Standard deviation = $\sqrt{\frac{\Sigma D^2}{n-1}} = \sqrt{\frac{17570.16}{5}} = 59.3$

Standard error = $S_X = \frac{S}{\sqrt{n}} = \frac{59.30}{\sqrt{6}} = 24.2$

Probable error = $S_X \cdot \frac{\sqrt{2}}{2} = (24.204)\ (0.7) = 16.9$

Per cent standard error = $\frac{24.204}{894.1} = 2.71\%$

Per cent probable error = $\frac{16.943}{894.1} = 1.89\%$

* 0.2 g. sample ppm (true) = (260 -93) ÷ 0.2 = 835 ppm/g.

Table 7. Analyses of molybdenite (medium level of rhenium) to show precision of the spectrographic standard addition method using the line at 3460.5 Angstrom units.

%T Re	%T Co	I_{Re}/I_{Co}	ppm obtained	ppm added	ppm/gram true	D	D^2
49.8	22.6	0.468	185	74.4	369*	0.7	0.49
50.5	24.1	0.482	192	"	392	22.3	497.29
44.8	26.5	0.605	245	139.5	350	19.7	388.09
41.6	23.9	0.610	250	"	367	2.7	7.29
35.2	22.3	0.695	287	186.0	337	32.7	1069.29
31.3	20.7	0.738	308	"	403	33.3	1108.89
Total					2218		3071.34
Average					369.7		

S = Standard deviation = $\sqrt{\frac{\Sigma D^2}{n-1}} = \sqrt{\frac{3071.34}{5}} = 24.8$

Standard error = $S_X = \frac{S}{\sqrt{n}} = \frac{24.83}{\sqrt{6}} = 10.1$

Probable error = $S_X \cdot \frac{\sqrt{2}}{2} = (10.135)\ (0.7) = 7.10$

Per cent standard error = $\frac{10.135}{369.7} = 2.74\%$

Per cent probable error = $\frac{7.095}{369.7} = 1.92\%$

* 0.3 g. sample ppm (true) = (185 -74.4) ÷ 0.3 = 369 ppm/g.

Table 8. Analyses of molybdenite (low level rhenium) to show precision of the spectrographic standard addition method using the line at 3460.5 Angstrom units.

%T Re	%T Co	I_{Re}/I_{Co}	ppm obtained	ppm added	ppm/gram true	D	D^2
80.0	26.1	0.168	61	18.6	85*	0.13	0.017
77.2	22.6	0.172	62	"	87	1.73	2.993
70.3	22.5	0.235	89	46.5	83	2.47	6.101
67.9	21.4	0.251	96	"	99	13.53	183.061
62.8	25.1	0.336	128	93.0	70	15.47	239.321
63.2	28.0	0.357	137	"	88	2.53	6.401
Total					512.8		437.894
Average					85.47		

$$S = \text{Standard deviation} = \sqrt{\frac{\Sigma D^2}{n-1}} = \sqrt{\frac{437.894}{5}} = 9.38$$

$$\text{Standard error} = S_{\bar{X}} = \frac{S}{\sqrt{n}} = \frac{9.38}{\sqrt{6}} = 3.83$$

$$\text{Probable error} = S_{\bar{X}} \cdot \frac{\sqrt{2}}{2} = (3.83)\,(0.7) = 2.68$$

$$\text{Per cent standard error} = \frac{3.83}{85.47} = 4.60\%$$

$$\text{Per cent probable error} = \frac{2.681}{85.47} = 3.13\%$$

* 0.5 g. sample ppm (true) = (61 -18.6) ÷ 0.5 = 85 ppm/g.

investigated. Further work led to the selection of lithium chloride as a buffer because it seemed to possess several of the desired characteristics. A typical calibration curve is shown in Fig. 3.

The buffer for the data reported in this paper was prepared by making 0.5 mole/liter solution of reagent grade lithium chloride. This solution was diluted with an equal volume of internal standard cobalt solution to give a final buffer concentration of 0.25 mole/liter.

Tables 9, 10 and 11 present results obtained when using a spectrographic buffer in the analyses of three sample ores of molybdenite. Tables 12, 13 and 14 show data obtained by the use of spectrographic buffer and standard addition method in the analyses.

COMPARISON OF SPECTROGRAPHIC ANALYSIS AND THIOCYANATE CHEMICAL METHOD

Before a spectrographic procedure can be accepted with any degree of confidence, it should undergo a favorable comparison with a well-known chemical procedure. The method used for comparison was identical to the widely used thiocyanate colorimetric procedure (10). A certain amount of sample (0.4, 0.5 and 1.0 g. of ores for high, medium and low levels of molybdenite respectively) was weighed and dissolved in nitric acid. The solution was evaporated to the stage at which a white precipitate began, 25 ml. of HCl was added, and the evaporation was repeated. The HCl evaporation was repeated three more times in order to remove nitric acid. Then 30 ml. of water was added, the solution was stirred, cooled, and transferred to a separatory funnel. Six ml. of 20 per cent KCNS solution was added, and the funnel was shaken; then 2 ml. of 25 per cent $SnCl_2$ (in 6 N HCl) solution was added, and the solution was shaken again.

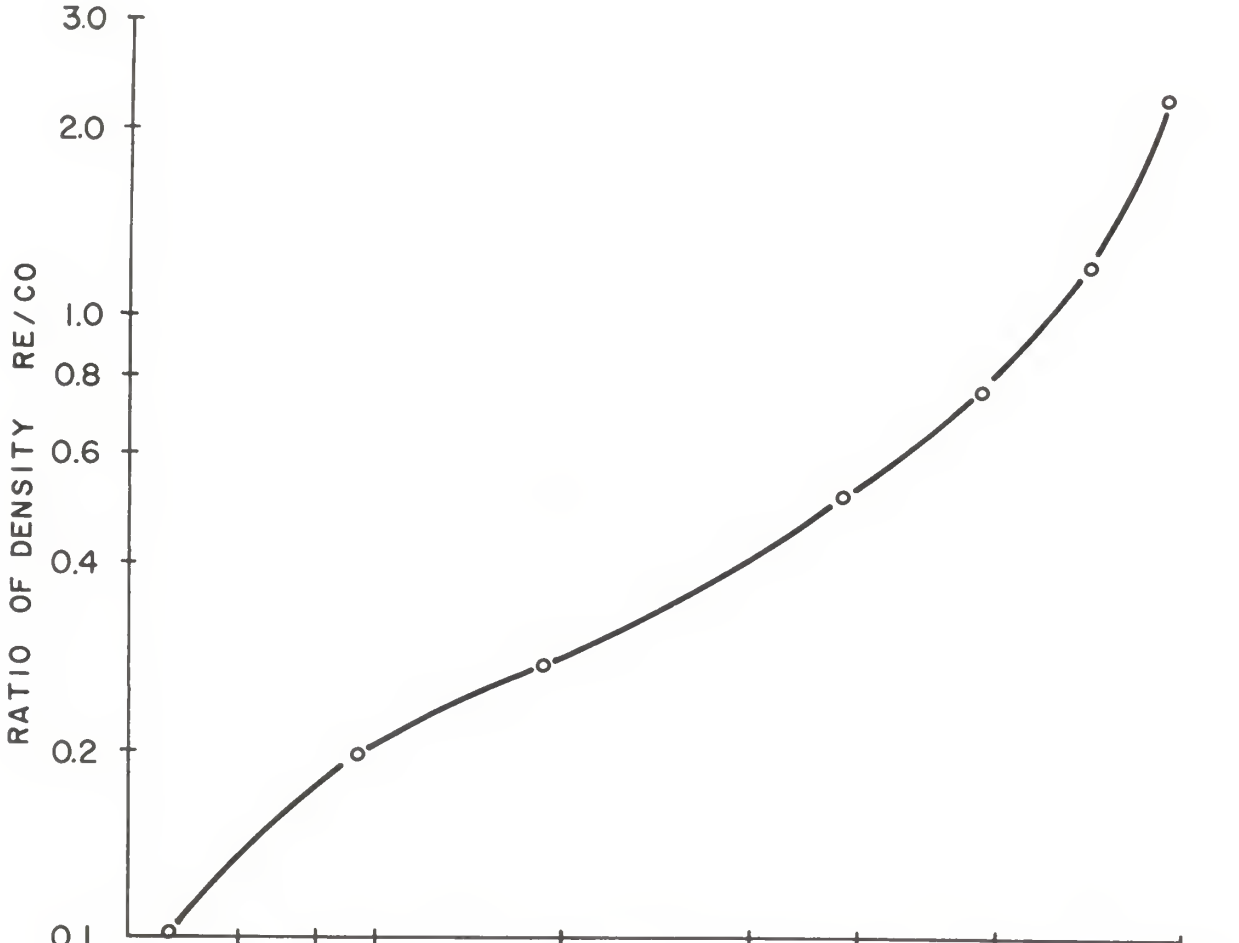

FIG. 3 WORKING CURVE OF RHENIUM WITH BUFFER

Table 9. Analyses of molybdenite (high level of rhenium) to show the precision of the spectrographic buffer method using the line at 3460.5 Angstrom units.

%T Re	%T Co	I_{Re}/I_{Co}	ppm/gram	D	D^2
55.1	20.4	0.374	833	66.3	4495.69
54.5	21.6	0.396	920	20.7	428.49
50.2	18.3	0.403	945	45.7	2088.49
Total			2698		7012.67
Average			899.3		

$$S = \text{Standard deviation} = \sqrt{\frac{\Sigma D^2}{n-1}} = \sqrt{\frac{7012.67}{2}} = 59.2$$

$$\text{Standard error} = S_X = \frac{S}{\sqrt{n}} = \frac{59.22}{\sqrt{3}} = 34.2$$

$$\text{Probable error} = S_X \cdot \frac{\sqrt{2}}{2} = (34.231)\ (0.7) = 24.0$$

$$\text{Per cent standard error} = \frac{34.231}{899.3} = 3.80\%$$

$$\text{Per cent probable error} = \frac{23.962}{899.3} = 2.65\%$$

Table 10. Analyses of molybdenite (medium level of rhenium) to show the precision of the spectrographic buffer method using the line at 3460.5 Angstrom units.

%T Re	%T Co	I_{Re}/I_{Co}	ppm/gram	D	D^2
64.3	19.6	0.270	364	53.3	2840.89
61.1	17.5	0.283	428	10.7	114.49
62.0	20.8	0.304	460	42.7	1823.29
Total			1252		4778.67
Average			417.3		

S = Standard deviation = $\sqrt{\frac{\Sigma D^2}{n-1}} = \sqrt{\frac{4778.67}{2}} = 48.9$

Standard error = $S_X = \frac{S}{\sqrt{n}} = \frac{48.88}{\sqrt{3}} = 28.3$

Probable error = $S_X \cdot \frac{\sqrt{2}}{2} = (28.253)\,(0.7) = 19.8$

Per cent standard error = $\frac{28.253}{417.3} = 6.77\%$

Per cent probable error = $\frac{19.777}{417.3} = 4.74\%$

Table 11. Analyses of molybdenite (low level of rhenium) to show the precision of the spectrographic buffer method using the line at 3460.5 Angstrom units.

%T Re	%T Co	I_{Re}/I_{Co}	ppm/gram	D	D^2
77.2	21.2	0.166	73.2	4.9	24.01
74.6	18.8	0.174	77.0	1.1	1.21
73.1	18.5	0.182	84.0	5.9	34.81
Total			234.2		60.03
Average			78.1		

$$S = \text{Standard deviation} = \sqrt{\frac{\sum D^2}{n-1}} = \sqrt{\frac{60.03}{2}} = 5.50$$

$$\text{Standard error} = S_X = \frac{S}{\sqrt{n}} = \frac{5.50}{\sqrt{3}} = 3.18$$

$$\text{Probable error} = S_X \cdot \frac{\sqrt{2}}{2} = (3.18)\ (0.7) = 2.23$$

$$\text{Per cent standard error} = \frac{3.18}{78.1} = 4.07\%$$

$$\text{Per cent probable error} = \frac{2.226}{78.1} = 2.85\%$$

Table 12. Analyses of molybdenite (high level of rhenium) to show the precision of the spectrographic standard addition method with buffer using the line at 3460.5 Angstrom units.

%T Re	%T Co	I_{Re}/I_{Co}	ppm obtained	ppm Added	ppm/gram true	D	D^2
62.3	25.2	0.330	268	93	875	47.5	2253.25
60.8	22.7	0.335	276	"	915	87.5	7656.25
54.2	20.0	0.378	340	186	770	57.5	3306.25
53.1	23.7	0.381	353	"	835	7.5	56.25
48.4	18.1	0.424	410	279	655	172.5	29756.25
52.5	24.3	0.456	460	"	905	77.5	6006.25
Total					4965		49283.50
Average					827.5		

S = Standard deviation = $\sqrt{\frac{\sum D^2}{n-1}} = \sqrt{\frac{49283.50}{5}} = 99.3$

Standard error = $S_X = \frac{S}{\sqrt{n}} = \frac{99.3}{\sqrt{6}} = 40.5$

Probable error = $S_X \cdot \frac{\sqrt{2}}{2} = (40.53)\ (0.7) = 28.4$

Per cent standard error = $\frac{40.53}{827.5} = 4.89\%$

Per cent probable error = $\frac{28.371}{827.5} = 3.43\%$

Table 13. Analyses of molybdenite (medium level rhenium) to show the precision of the spectrographic standard addition method with buffer using the line at 3460.5 Angstrom units.

%T Re	%T Co	I_{Re}/I_{Co}	ppm obtained	ppm added	ppm/gram true	D	D^2
66.2	22.6	0.278	194	74.4	399	30.5	930.25
68.0	25.4	0.281	196	"	405	36.5	1332.25
62.5	21.2	0.302	227	139.5	292	76.5	5852.25
64.7	24.8	0.314	245	"	352	15.5	240.25
55.1	18.7	0.355	305	186.0	397	28.5	812.25
56.8	21.5	0.369	326	"	466	97.5	9506.25
Total					2211		18667.50
Average					368.5		

$$S = \text{Standard deviation} = \sqrt{\frac{\sum D^2}{n-1}} = \sqrt{\frac{18667.50}{5}} = 61.1$$

$$\text{Standard error} = S_X = \frac{S}{\sqrt{n}} = \frac{61.12}{\sqrt{6}} = 24.9$$

$$\text{Probable error} = S_X \cdot \frac{\sqrt{2}}{2} = (24.946)\ (0.7) = 17.5$$

$$\text{Per cent standard error} = \frac{24.946}{368.5} = 6.77\%$$

$$\text{Per cent probable error} = \frac{17.462}{368.5} = 4.74\%$$

Table 14. Analyses of molybdenite (low level rhenium) to show the precision of the spectrographic standard addition method with buffer using the line at 3460.5 Angstrom units.

%T Re	%T Co	I_{Re}/I_{Co}	ppm obtained	ppm added	ppm/gram true	D	D^2
77.5	17.6	0.146	64	18.6	91	6.2	38.44
79.2	21.4	0.149	65	"	94	9.2	84.64
73.5	19.8	0.191	88	46.5	83	1.8	3.24
72.6	19.0	0.193	90	"	87	2.2	4.84
70.8	22.1	0.229	124	93.0	62	22.8	519.84
67.9	20.2	0.242	139	"	92	7.2	51.84
Total					509		702.84
Average					84.8		

$$S = \text{Standard deviation} = \sqrt{\frac{\Sigma D^2}{n-1}} = \sqrt{\frac{702.84}{5}} = 11.9$$

$$\text{Standard error} = S_X = \frac{S}{\sqrt{n}} = \frac{11.85}{\sqrt{6}} = 4.83$$

$$\text{Probable error} = S_X \cdot \frac{\sqrt{2}}{2} = (4.83)\,(0.7) = 3.38$$

$$\text{Per cent standard error} = \frac{4.83}{84.8} = 5.69\%$$

$$\text{Per cent probable error} = \frac{3.381}{84.8} = 3.98\%$$

Following this, 15 ml. of amyl alcohol was added and the solution was shaken vigorously. The extractions on the aqeous layer were repeated a second and a third time, using 10 ml. quantities of amyl alcohol and adding the extracts together. The extractant was shaken three times with 5 ml. of dilute HCl, and the aqueous layer was discarded in order to remove most of the uranyl and stannous chlorides dissolved in the amyl alcohol. The amyl alcohol solution was evaporated carefully to a volume of about 2 ml. which was then allowed to cool; about 1 ml. of nitric acid was then cautiously added. After the initial vigorous reaction had subsided, another 5 ml. of nitric acid was added, and the solution was gently heated in order to complete the oxidation. Ten ml. of HCl was added, and the solution was then evaporated to 2 ml. This process was repeated three times to remove nitric acid. The solution was then diluted with 25 ml. of water, and 1 g. of cupferron in 10 ml. of water was added, and then filtered, the precipitate being allowed to drain. The filtrate was extracted with 3 successive 20 ml. portions of $CHCl_3$. Ten ml. of HCl was added, the solution was extracted twice with 20 ml. portions of $CHCl_3$, and the $CHCl_3$ extracts were discarded. Six ml. of KCNS solution and 2 ml. of $SnCl_2$ solution were added to the aqueous layer, which was then shaken and extracted with 8 ml. of amyl alcohol extract, containing any rhenium as thiocyanate complex, was diluted to 10 ml. The orange yellow color of the amyl alcohol was measured by using a Beckman DU Spectrophotometer at a wavelength of 340 mμ. The concentration of rhenium was determined by comparison with the curve shown in Fig. 4.

A series of three molybdenite samples were analyzed by this method and compared with the spectrographic analysis using the rhenium line at 3460.5 Angstrom units. The results are tabulated in Table 16. Examination of the

data shows a maximum deviation of 14.12 per cent and the average deviation being 90.82 ppm for the high level of molybdenite; a maximum deviation of 16.63 per cent and the average deviation being 51.62 ppm for the medium level; and a maximum deviation of 13.22 per cent and the average deviation of 6.81 ppm for the low level.

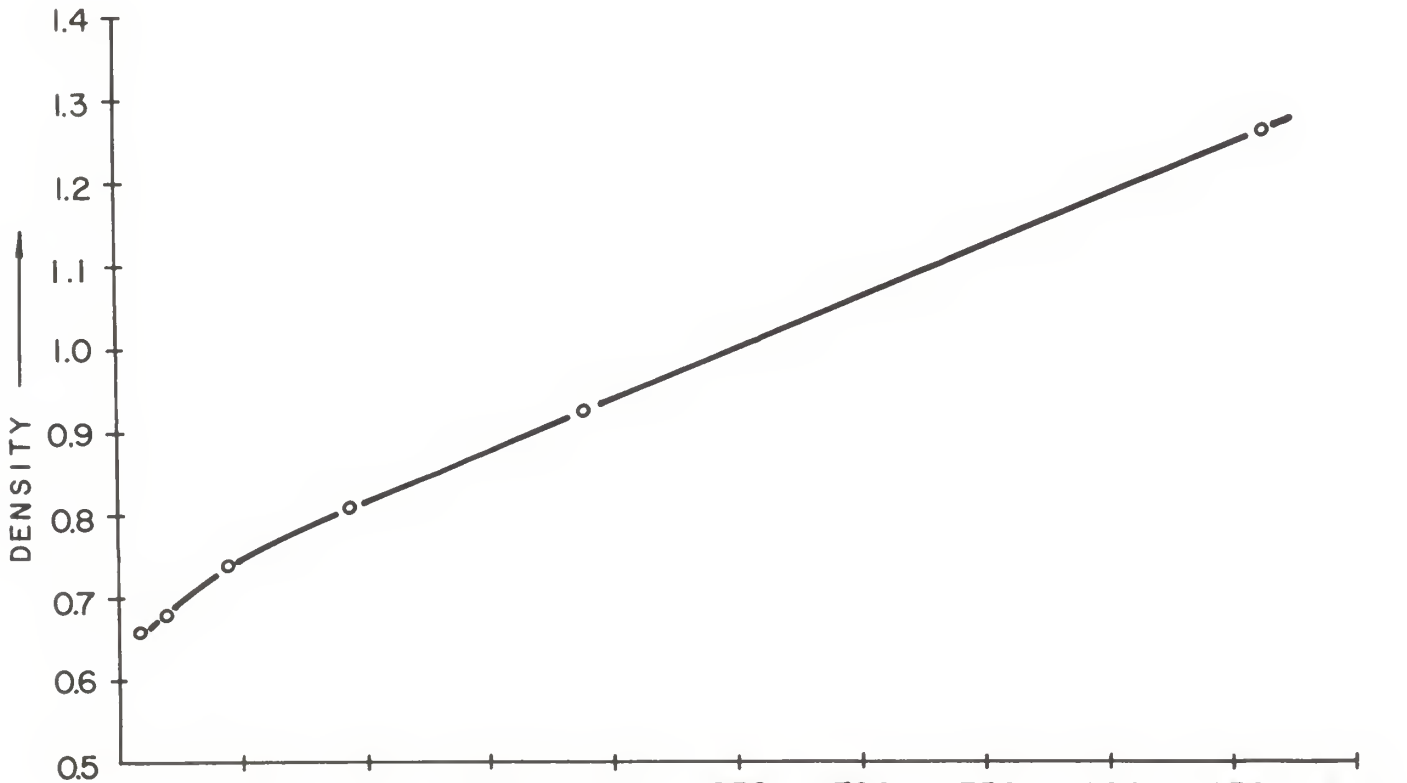

FIG. 4 COLORIMETRIC WORKING CURVE

Table 15. Comparison of spectrographic and thiocyanate methods of analysis of molybdenite for rhenium using the line at 3460.5 Angstrom units.

Sample	Thiocyanate ppm	Spectrographic ppm	Deviation ppm	Per cent deviation
High level	950			
Without buffer	"	815.8	-134.2	-14.12
Standard addition	"	894.1	-55.9	-5.86
With buffer	"	899.3	-50.7	-5.33
Standard addition	"	827.5	-122.5	-12.89
Medium level	442			
Without buffer	"	406.8	-35.2	-7.96
Standard addition	"	369.7	-72.3	-16.35
With buffer	"	417.3	-24.7	-5.58
Standard addition	"	368.5	-73.5	-16.63
Low level	90			
Without buffer	"	84.4	-5.6	-6.22
Standard addition	"	85.5	-4.5	-5.02
With buffer	"	78.1	-11.9	-13.22
Standard addition	"	84.8	-5.2	-5.78

CONCLUSIONS

A spectrographic procedure of good precision for the determination of rhenium in molybdenite has been developed. The procedure made use of a quaternary amine complex with perrhenate and 4-methyl-2-pentanone extraction to separate rhenium from the interfering elements and concentrate the rhenium, and lithium chloride as a buffer to suppress variations due to differences in composition and to stabilize the d.c. arc. Cobalt was used as the internal standard.

The precision of this method showed a probable error of less than 5 per cent when using the rhenium line at 3460.5 A. The value compared satisfactorily with the thiocyanate colorimetric procedure, the average deviation being about 10 per cent less than the chemically determined value.

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SPECTROGRAPHIC DETERMINATION OF RHENIUM IN MOLYBDENITE WITH THE D.C. ARC

by

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B. S., National Taiwan University, 1961

AN ABSTRACT OF A MASTER'S THESIS

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ABSTRACT

The quantitative determination of rhenium in molybdenite ores is complicated due to (1) its low concentration and (2) the presence of interfering elements. A variety of chemical separations of rhenium from molybdenite have been developed, none of them completely satisfactory. Among the separation procedures reported in the literature are distillation, differential reduction, extraction, and ion exchange. Application of colorimetric methods to rhenium separated by the above methods has been difficult since the color producing agents have been non-specific.

This research was carried out to evaluate the usefulness of spectrographic procedures for the determination of rhenium in molybdenite. Preliminary concentration of rhenium was found necessary. The following concentration procedure was developed and found satisfactory.

Samples were placed in solution with HNO_3 and evaporated to dryness. The residue was taken up in HCl, filtered, and the filtrate was evaporated. Excess NH_4OH was added and the solution filtered. The filtrate was evaporated to two ml. Two ml. of a concentrated solution of NaOH (10 M) and 2 ml. of 0.1 M tetrabutyl ammonium bromide were added. Extraction of the rhenium from the above solution was accomplished with successive treatments with 4-methyl-2-pentanone. The extracts were evaporated to dryness and taken up in 0.1 N HCl. Cobalt was used as the internal standard, and lithium chloride as a buffer to suppress variations due to differences in composition and to stabilize the d.c. arc.

The spectrograph used was a Bausch and Lomb large Littrow instrument with quartz optics. Eastman type spectrographic analysis No. 1 plates were used. The samples were arced with a d.c. potential of 150 volts and a cur-

rent of 12.5 amperes for a period of 30 seconds. After exposure the plates were developed for five minutes at 68°F in Eastman D-19 developer, then fixed, washed and dried. Line intensities were obtained by means of an Allied Research Laboratories-Dietert densitometer. The rhenium line at 3460.5 Å was used with the cobalt line at 3453 Å serving as internal standard.

The precision of the method was determined by a series of analyses on three different molybdenite samples. The ores contained 816, 407, and 84.4 ppm of rhenium respectivrly. The spectrographic precision showed an average probable error of less than four percent. Standard addition techniques indicated complete recovery of rhenium. Comparison with the thiocyanate colorimetric procedure gave values for the spectrographic method that average about ten percent below the chemically determined value.