Circular 108

Analysis of Rhenium in Molybdenites

by LORNA M. GOEBEL

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Associate Curator, Corpus Christi Museum

1970

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ABSTRACT

Current procedures for the analysis of rhenium are based on separation methods that fail to isolate rhenium from interfering elements. Of several analytical methods studied, calcining with calcium oxide, leaching with a hot aqueous oxidizing solution, and spectrophotometrically determining the concentration of rhenium with a-furildioxime produces the most reliable results. Using this procedure, a sample of Arizona molybdenite concentrate was shown to contain 320 ppm rhenium with a 95-percent confidence interval of 10 ppm and a standard deviation of 4.97 percent; standard deviations as low as 0.79 percent were obtained on single runs of four or more replicates. Published standard deviations for conventional analyses of the same material average about 20 percent. Recovery of 90 to 100 percent of added standards was obtained up to a total rhenium content of 500 ppm for a 1-g sample.

INTRODUCTION

The current (1969) procedures for the analysis of rhenium are based on separation methods that do not completely isolate rhenium from interfering elements, especially molybdenum. Geilmann, Weigge, and Weibke (1932) devised the potassium thiocyanate-stannous chloride ($KCNS\text{-}SnCl_2$) spectrophotometric method, which, with some modifications, has been considered the best method for determining rhenium content.

Lebedev (1962) reported that Suvorova, Burdokov, and Rashii calcined molybdenite concentrates with calcium oxide (CaO) to form calcium perrhenate ($Ca[ReO_4]_2$). If rhenium in molybdenite is assumed in the stoichiometric ratio of ReS_2 (Lebedev, 1962), then the roasting with calcium oxide is given by the equations:

$$4\ ReS_2 + 15\ O_2 \rightarrow 2\ Re_2O_7 + 8\ SO_2$$

and

$$Re_2O_7 + CaO \rightarrow Ca(ReO_4)_2$$

and the over-all reaction is

$$4\ ReS_2 + 2\ CaO + 15\ O_2 \rightarrow 2\ Ca(ReO_4)_2 + 8\ SO_2$$

In the absence of excess oxygen, the sulfur dioxide will reduce the heptoxide to rhenium dioxide and rhenium trioxide. To prevent this, the use of oxidizing agents mixed with the lime has been proposed; calcium nitrate (Tsyvina and Davidovich, 1960), potassium perchlorate (Peshkova, Ignat'eva, and Ozerova, 1963), and potassium permanganate (Nikolaeva and Stolyarova, 1964) have been used in this respect.

The solubility of calcium perrhenate dihydrate ($Ca[ReO_4]_2 \cdot 2\ H_2O$) is 227.8 g/100 ml of water at 30°C (Smith and Maxwell, 1951), whereas that of calcium molybdate ($CaMoO_4$) is only 0.0023 g/ 100 ml at 20°C (Siedell and Linke, 1952). At 1 atmosphere the dissociation pressure of calcium perrhenate ranges from 0.03 mm Hg at 600°C to 0.157 mm Hg at 720°C. Hence, by calcining a sample with calcium oxide (lime) and water-leaching the roasted cake, a quantitative separation of rhenium and molybdenum should be effected. Tsyvina and Davidovich (1960), using radioactive rhenium-186 as a tracer, reported up to 96 percent recovery with the calcium oxide roast at 600° to 800°C. They and Peshkova, Ignat'eva, and Ozerova (1963) removed the sulfate ion by precipitation with barium chloride. Nikolaeva and Stolya-

rova (1964) removed excess calcium ion by precipitation with ammonium carbonate. Using these procedures, rhenium may be effectively separated from the following ions that interfere with a spectrophotometric determination: molybdenum, tungsten, calcium, cadmium, bismuth, antimony, mercury, selenium, tellurium, and arsenic.

Of the many reagents that have been suggested for the spectrophotometric determination of rhenium, the two most widely used are thiocyanate ion and a-furildioxime. Perrhenate ion, on reduction with stannous chloride, yields a reactive complex, $ReO_2C1_2^{-3}$ (Iordanov and Pavlova, 1967). The reaction of perrhenate ion with a -furildioxime was first reported by Peshkova and Gromova (1952), who found that perrhenate, in the presence of stannous chloride with a -furildioxime, forms solutions that are yellow orange, orange, or raspberry red, depending on the quantities of reagents. This suggests the formation of different complexes. The red compound is extractable with organic solvents and the resulting solutions obey Beer's law. The maximum absorption is at 533 millimicrons, with a specific absorbance at 530 millimicrons of 3.39×10^4 (Pollock and Zopatti, 1965). Meloche, Martin, and Webb (1957) were the first to publish a procedure using a-furildioxime and reported that in the range of 0.4 to 6.0 ppm rhenium the absorbance follows Beer's law with an average deviation of +0.2 percent(?). Toul and Okác (1960) and Heaney and Malouf (1963) studied interferences and reported that bismuth, chromium, tungsten, vanadium, cupric molybdate, arsenite, arsenate, selenate, nitrate, and thiocyanate ions, noble metals, and oxidizing agents interfere. Molybdenum causes low values by forming colorless compounds, but appears to be tolerated to a greater extent than in the thiocyanate method.

In this investigation, published procedures for determination of rhenium in molybdenum concentrates were reviewed and compared experimentally, and an improved method was devised.

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EXPERIMENTAL PROCEDURES

Reagents

Calcium oxide, CaO, technical grade.

Potassium permanganate, $KMnO_4$, reagent grade, 1-percent aqueous solution.

Barium chloride, $BaCl_2$, reagent grade, 0.5M aqueous solution.

Ammonium carbonate, $(NH_4)_2CO_3$, 250 g in enough 6N NH4OH to make 1 liter.

a-furildioxime, $(C_4H_3O{\bullet}C{:}NOH)_2{\bullet}2H_2O$, C. P. grade, 0.7 g in 200 ml acetone, made fresh.

Stannous chloride, $SnCl_2{\bullet}\ 2H_20$, reagent grade, 10 g dissolved in 10 ml concentrated hydrochloric acid diluted to 100 ml, made fresh.

Ammonium perrhenate, NH_4ReO_4, C. P. grade, 1,000 ppm aqueous stock solution, diluted as needed.

Samples

Four flotation concentrates of molybdenite, MoS, and one commercial molybdenite reagent were used for standards aria' test materials, as follows:

A. Arizona molybdenite concentrate; rhenium content high. This sample was used for comparative study of methods.
B. New Mexico molybdenite concentrate; 10 ppm rhenium (Fleischer, 1959).
C. Colorado molybdenite concentrate; 5 to 28 ppm rhenium (Fleischer, 1959).
D. New Mexico molybdenite concentrate; 18 ppm rhenium (Fleischer, 1959).
E. E. Arizona molybdenite concentrate; analysis not published.
F. Southwestern United States molybdenite concentrate; 370 ppm rhenium (private, communication).
G. Molybdenite reagent; Sargent Chemical Company, Lot SC 13658.

Procedure

Mix intimately a 1-g sample of molybdenite concentrate and about 3 g calcium oxide, and cover the mixture with enough calcium oxide to fill a tall-form Coors porcelain crucible (size 1A) to within 1 cm of the top (about 10 g). Cover crucible, place in a cold muffle, and bring to roasting temperature of 700°C for 4 hours. After cooling, transfer calcined cake to a 400-

ml beaker. Rinse crucible with distilled water and add rinsing to the beaker. If a brownish or blackish spot remains on the crucible, dissolve with a drop of potassium permanganate solution and add to beaker. Increase volume to about 200 ml by adding distilled water and bring to a boil. Stir while adding potassium permanganate solution a drop at a time until the color persists at least 30 seconds. Boil the solution gently for about 0.5 hour, adding water as needed to maintain the volume above 100 ml. Filter the sample through a Buchner funnel, washing thoroughly with boiling distilled water. Evaporate the filtrate to a volume of about 50 ml. Add 5 ml barium chloride solution and heat to boil. Add 5 ml ammonium carbonate solution and heat to boil; continue boiling for 2 to 4 minutes. Caution: prolonged boiling at this point may cause the re-solution of some sulfate. Filter through What-man 42 filter paper into a 100-m1 volumetric flask. Wash the precipitate thoroughly with hot distilled water, cool, make up to volume and mix. If any sediment forms, allow it to settle before taking a sample aliquot.

To develop color, place a 10-m1 aliquot of the leach solution in a 25-ml volumetric flask and add 1.5 ml of concentrated hydrochloric acid, 6.5 ml of a-furildioxime solution and, immediately, 2.5 ml stannous chloride solution. (If the stannous chloride is not added quickly, the reaction of the -furildioxime will produce color differences that yield low values; Peshkova and Gromova, 1952.) Dilute at once to 25 ml, stopper, and shake vigorously for 20 seconds; the immediate addition of water and thorough mixing will prevent the formation of a white opalescence and a consequently misleading increase in absorption. After 35 minutes, read the absorbance at 532 millimicrons and determine concentration from a standard calibration curve as percent rhenium or ppm rhenium.

RESULTS AND DISCUSSION

Table 1 is a comparison of the different procedures used in the analysis of molybdenite-concentrate sample A. The emission spectrograph (ARL 26100) gave a semiquantitative value of 800 ppm rhenium, with an estimated reproducibility of 50 percent. X-ray fluorescence (Norelco) gave a value of 300 ppm rhenium, with an estimated error of 10 to 15 percent.

Rhenium in an acidic oxidizing solution forms perrhenic acid, $HReO_4$, which will volatilize above 80°C, an ever-present danger in acid solution techniques. The fuming nitric acid procedure of Sandell (1959), which is

TABLE 1

COMPARISON OF METHODS

Sample A

Method	No. of samples	Rhenium content (ppm)	Standard deviation (%)
Emission spectrograph	1	800	±50*
X-ray fluorescence	1	300	±10-15*
Fuming nitric acid¶	14	508	18.72
Concentrated nitric acid¶	15	365	27.01
NaOCl leach¶	14	389	16.30
NaOH-Na_2O_2 fusion¶	15	429	7.01
CaO roast, $KMnO_4$ in roast§	10	327	10.05
CaO roast, no $KMnO_4$§	30	320	4.97

* Estimated instrumental error.
V Spectrophotometric determination with thiocyanate; 430 millimicrons.
§ Spectrophotometric determination with a-furildioxime; 530 millimicrons.

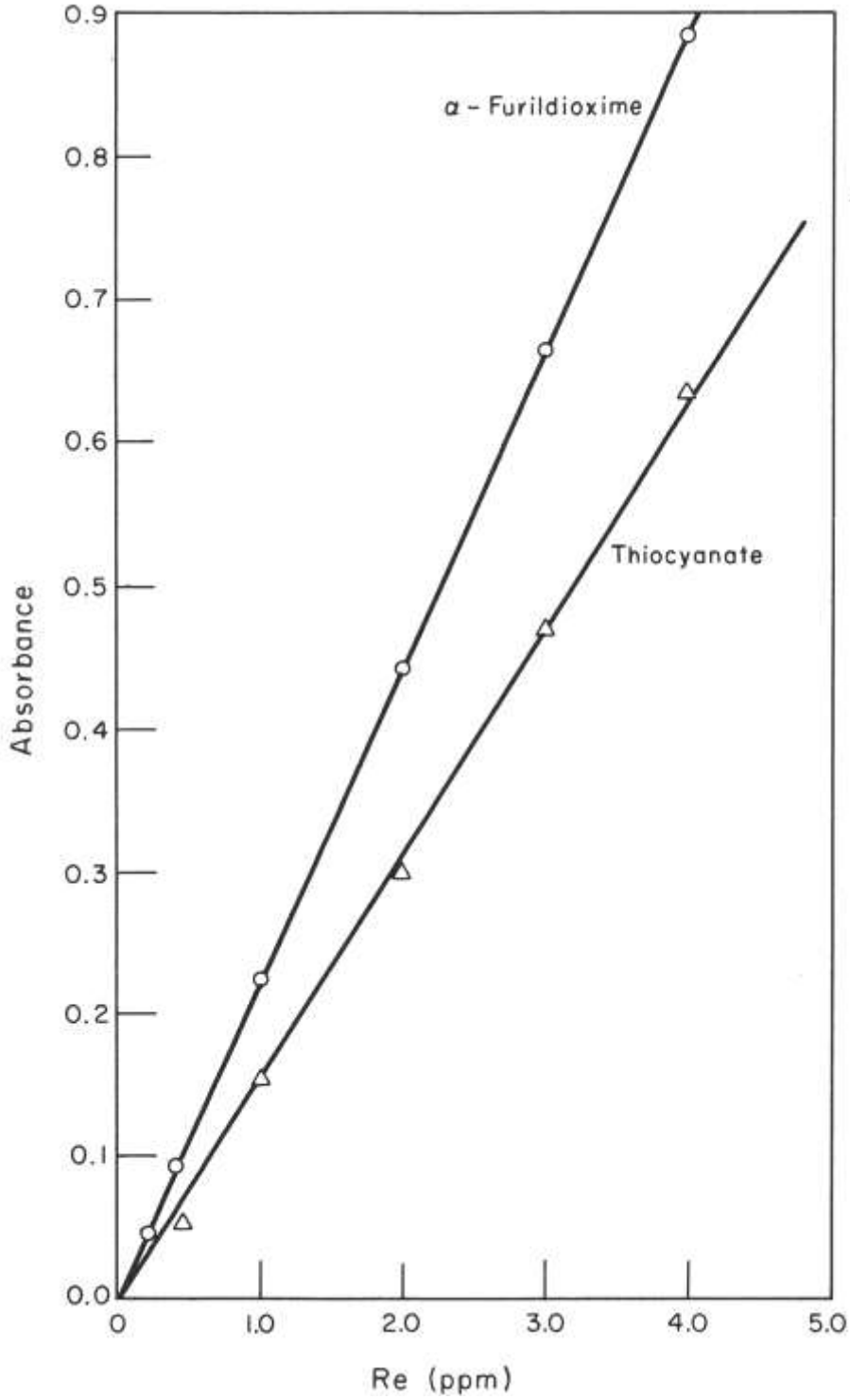

Figure 1. Standard calibration curves for spectro - photometric determinations using **a** -furildioxime and thiocyanate complexes.

TABLE 2

DEVELOPMENT OF THE CALCIUM OXIDE ROAST PROCEDURE

Sample A

Run	No. of samples	Concentration (ppm)	$KMnO_4$ in roast (g)	Leach	CaO (g)	Temp. (°C)	Time (hrs)
1	11	154±7	0.0	cold	3	600	2
2	3	95±6	0.01	"	3	600	2
3	3	77±6	0.05	"	3	600	2
4	3	81±12	0.10	"	3	600	2
5	3	163±2	0.01	hot	3	600	2
6	8	180±6	0.01	"	6	600	2
7[a]	2	197±16	1.01	"	3	600	2
8[b]	2	226±9	1.01	"	3	600	2
9[a,b]	2	231±6	1.01	"	3	600	2
10[a,b]	10	327±33	0.4	"	13	700	4
11[a,b]	30	320±16	0.0	"	13	700	4
12[a,b]	4	333±16	0.0	"	13	700	2

a Calcium removed with ammonium carbonate.
b Sulfate removed with barium chloride.

generally considered one of the best methods of rhenium analysis, gave a value for sample A of 508+95 ppm rhenium. The concentrated nitric acid method, which is the same procedure using laboratory acid in place of fuming nitric acid, gave a somewhat lower value of 365+99 ppm rhenium. Both methods involve an evaporation step that must be performed on a steam bath and takes from 48 to 72 hours. In these procedures the rhenium is separated from interfering ions by extracting tetraphenylarsonium perrhenate into chloroform, then back-extracting into 6N hydrochloric acid, and determining the concentration of rhenium by the thiocyanate spectrophotometric method as outlined by Sandell (1959). The values are believed to be high.

By another method the samples were leached with sodium hypochlo-

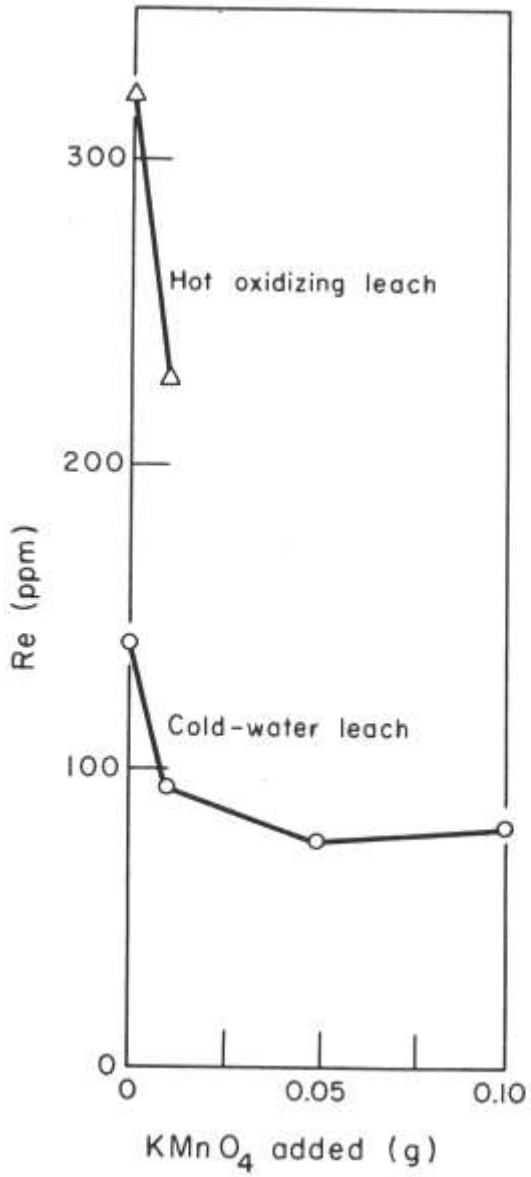

Figure 2. Effect of $KMnO_4$ in roast

rite (Clorox) solution buffered to pH 9.5+0.1, followed by extraction into chloroform as tetraphenylarsonium perrhenate. The rhenium content was measured spectrophotometrically by Sandell's thiocyanate procedure. An average of 389+63 ppm rhenium was obtained for sample A. The values from this method also appear to be high.

Samples of molybdenite concentrate were also fused with a 3:1 mixture of sodium hydroxide and sodium peroxide according to the procedure of Peterson, MacDuff, and Hovey (1961). This method assures that all of the rhenium will be in the heptavalent, Re(VII), state. The fused samples were dissolved in water and subjected to the extraction procedure and the thiocya-

nate colorimetric determination. This method gave a value of 429+30 ppm rhenium for sample A, which also appears to be high.

When the rhenium is extracted into chloroform as tetraphenylarsonium perrhenate and analyzed as the thiocyanate complex, values tend to be high (table 1) because the spectrophotometric procedure is extremely sensitive to molybdenum. (All of the values that could be rejected statistically have been high values.) Despite favorable published distribution coefficients for this extraction procedure, significant errors arise from the failure to separate all of the molybdenum from rhenium.

After comparing the thiocyanate method of Sandell and the a -furildioxime procedure of Meloche, Martin, and Webb (1957), the latter was chosen for use with the calcium oxide roast because it is more sensitive and appears to be more reliable. Comparative data for the two procedures are shown in Figure 1,

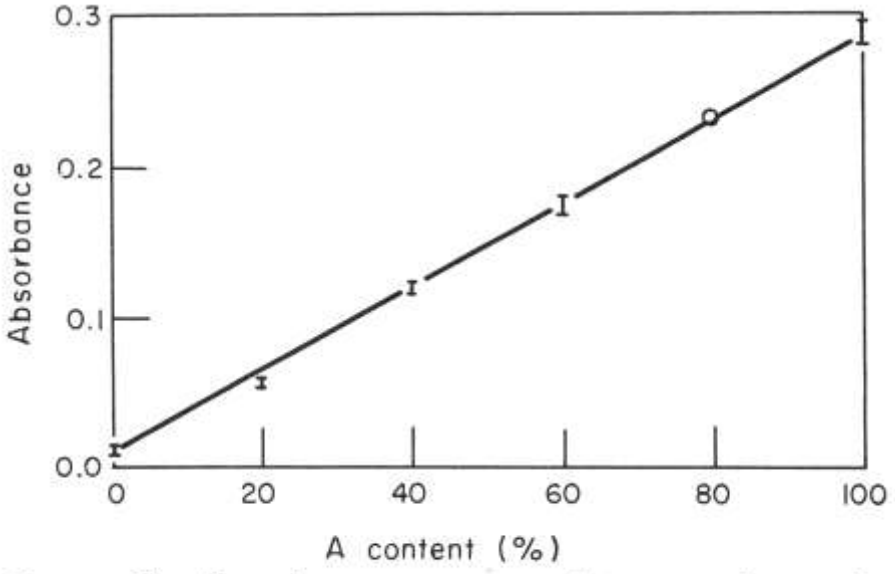

Figure 3. Absorbance versus mixtures of samples A and C.

The calcium oxide roast procedure as described in the Russian literature* was investigated as listed in Table 2. The initial run was made with 3 g calcium oxide to 1 g molybdenite concentrate instead of the recommended 1.5 to 1.0 ratio. Compared to other methods, the calcium oxide roast gave low values. Since it is possible that all the rhenium was not being oxidized to the heptavalent state, potassium permanganate was added to the mix be-

Lebedev, 1962; Tsyvina and Davidovich, 1960; Nikolaeva and Stolyarova, 1964; Fleischer, 1959.

fore roasting. Runs 2, 3, and 4 (table 2; fig. 2) indicate that the additions resulted in even lower values. Subsequent runs were made with .a small amount (0.01 g permanganate), but in the final method no oxidant was added before roasting. The reaction of the rhenium heptoxide with calcium oxide is probably a two-phase, gas-solid reaction because the heptoxide volatilizes at 450°C, well below roasting temperatures. Despite thorough mixing and a covering of lime, apparently the heptoxide was produced too rapidly to react completely with the calcium oxide.

Cold water was used to leach the roasted sample for the first four runs. As shown by runs 2 and 5, a considerably higher value was obtained by leaching with hot water to which potassium permanganate had been added to insure complete oxidation of rhenium. Comparison of runs 7 and 5 shows

TABLE 3

REPETITIVE RUNS WITH FINAL PROCEDURE

Sample A

Run	No. of samples	Average Re content (ppm)	Standard deviation (%)	Absolute range (ppm)	95-percent confidence interval (ppm)
1	4	319	0.79	5	4
2	5	309	4.06	35	18
3	3	309	2.92	18	23
4	3	301	3.00	18	23
5	3	344	2.86	17	22
6	3	335	1.49	5	6
7	3	320	5.30	24	154
8	3	331	3.08	20	26
9	2	312	5.67	24	154
10	2	324	6.11	28	179
Avg.	30	320	4.97	65	10
2-hr Run					
Avg.	4	333	4.77	37	27

TABLE 4

RECOVERY EXPERIMENTS

Mixed Samples
Sample A added to Sample C

Sample weight ratios C:A	Absorbance	Indicated Re content* (ppm)	Indicated recovery* (%)
1:0	0.010	1±1	-
2:1	0.055	67±3	95.5
3:2	0.118	137±7	100.0
2:3	0.176	198±10	97.4
1:4	0.233	266±13	98.8
0:1	0.288	327±16	-

Added Standards
Ammonium perrhenate added to Sample A

Added Re (ppm)	Absorbance	Indicated Re content* (ppm)	Indicated recovery* (%)
0	0.272	310	-
50	0.310	352	84.0
100	0.358	408	99.0
150	0.405	460	100.0
250	0.470	535	90.0
300	0.510	580	90.0
500	0.620	705	79.0

*Value obtained from ammonium perrhenate standard curve.

that results are improved by removal of calcium ions. When the sulfate ion alone was removed, as in run 8, an even higher value was observed. Removal of both calcium and sulfate ions (run 9) resulted in still higher values. In the final procedure, sulfate ions were removed by addition of barium chloride, and calcium ions and excess barium ions were removed by precipitation with ammonium carbonate.

Even with the hot oxidizing leach and removal of both calcium and sulfate (run 9) the results are still lower than indicated by x-ray fluorescence. Comparison of the results from runs 6 and 5 suggested the need for a larger amount of calcium oxide, and, in run 10, 13 g of calcium oxide was added to 1-g samples that were mixed with 0.4 g potassium permanganate. These samples were then calcined at 700°C for 4 hours. Run 10 shows an average of 327+33 ppm rhenium for this procedure. This value compares favorably with the value indicated by x-ray fluorescence, but the deviation

was higher than for the earlier runs. To determine the effect of potassium permanganate in the roasting step, run 11 was made with 1-g samples mixed with 13 g calcium oxide and without potassium permanganate; roasting was at 700°C for 4 hours. The results averaged 320+16 ppm rhenium. This modification was adopted for the final procedure.

Using the final procedure, the rhenium content of molybdenite-concentrate sample A was determined to be 320+16 ppm (C.I. (95%) +10 ppm). This value is the average of 30 analyses distributed in 10 separate runs (table 3).

Table 4 shows the results of a recovery study conducted in two

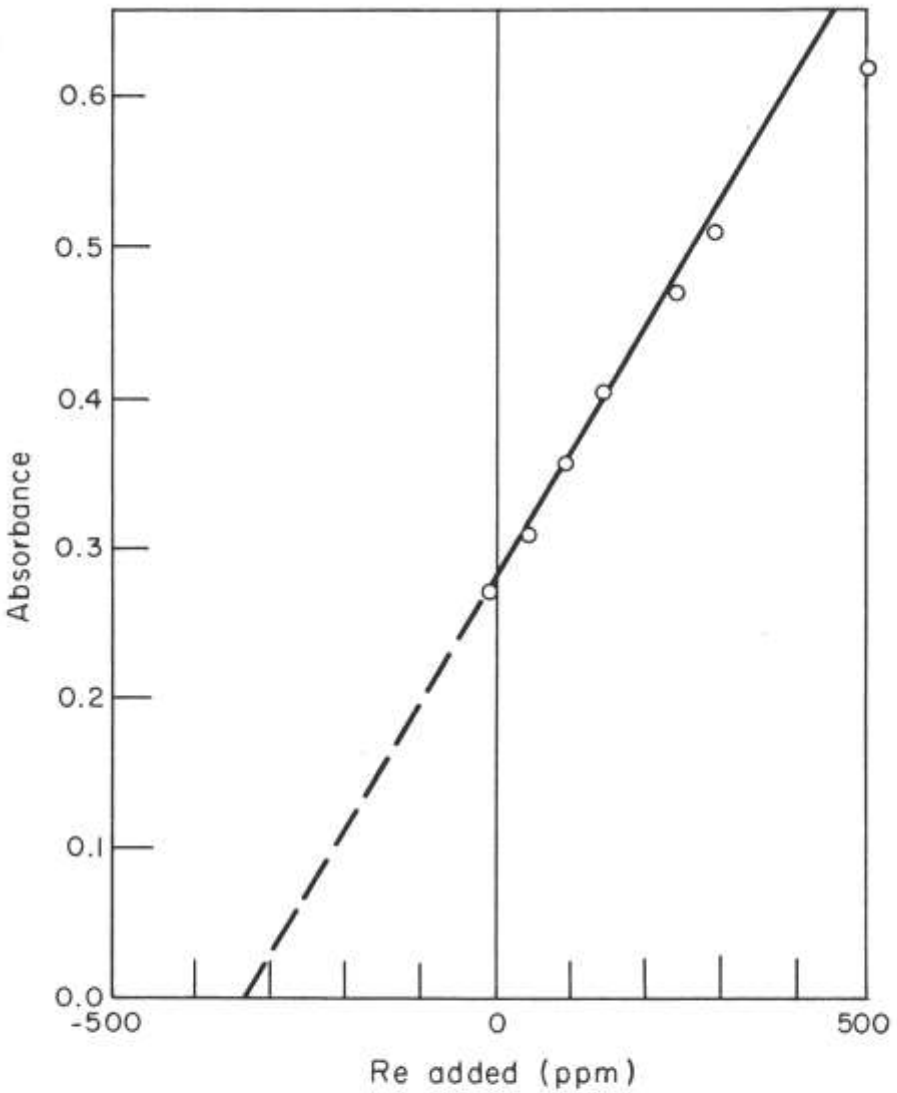

Figure 4. Absorbance as a function of addition of rhenium (as NH_4ReO_4) added to sample A.

RHENIUM CONTENT IN MOLYBDENITES

Sample	No. of analyses	Average (ppm)	Standard deviation (%)	X-ray fluor.	Published value (ppm)
A	30	320	4.97	300	-
B	4	30	8.16	-	8-12*
C	7	2	167.7	5	5-28*
D	4	348	2.01	-	18*
E	4	121	3.27	-	-
F	4	143	10.16	130	370**
G	4	137	7.03	-	-

*Fleisher, 1959.
**Private communication.

phases: (1) dilution of sample A by mixing with a molybdenite of low rhenium content (sample C; about 2 ppm as analyzed by final procedure) and (2) enrichment of sample A by addition of ammonium perrhenate. The results are plotted in Figures 3 and 4. The values fall on a straight line for the diluted samples but on a slight curve of lower slope for the enriched samples. Recoveries of 90 to 100 percent of added standards were obtained up to a total rhenium content of 500 ppm for a 1-g sample.

Table 5 shows the values obtained for the rhenium content of the six molybdenite concentrates from Arizona, Colorado, and New Mexico, and the molybdenite reagent.

SUMMARY AND CONCLUSIONS

The semiquantitative spectrographic determination of rhenium content of molybdenite concentrates is unsatisfactory, whereas the x-ray fluorescence method appears to be correct within 10 to 15 percent of the amount present and is useful to screen samples. Dissolution methods investigated were fuming nitric acid, concentrated nitric acid, sodium hydroxide-sodium peroxide fusion, sodium hypochlorite, and a calcium oxide roast. For the first four dissolution methods rhenium was separated from molybdenum by extraction as tetraphenylarsonium perrhenate into chloroform.

Spectrophotometric determinations of rhenium content by the rhenium-thiocyanate method at 430 millimicrons appear to be high, presumably because traces of molybdenum are carried through the extraction step. Spectrophotometric determinations by the rhenium-a -furildioxime method at 530 millimicrons are more dependable.

A satisfactory procedure for analyzing rhenium in a molybdenite concentrate is a calcium oxide roast at 700°C for 4 hours, followed by leaching with boiling distilled water to which 1 percent potassium permanganate solution is added by small increments until the color persists for at least 30 seconds. After removing sulfate and excess calcium, the concentration of rhenium is then determined spectrophotometrically using a rhenium-a-furildioxime complex at 530 millimicrons. Recovery of 90 to 100 percent of added standards was obtained up to a total rhenium content of 500 ppm for a 1-g sample. Results show a 95 percent confidence interval of 3. 1 percent and a standard deviation of 5 percent.

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