PLASMA ARC EXCITATION FOR THE SPECTROGRAPHIC
DETERMINATION OF RHENIUM

by

COLETTE WEN-LI CHANG

B. S., Mount Saint Scholastica College, 1963

———————

A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1965

Approved by:

W. G. Schrenk
Major Professor

TABLE OF CONTENTS

INTRODUCTION

The accomplishments achieved by scientists through use of
the spectrograph form a list so imposing as to leave no doubt
that this instrument is one of the most important now available
for investigating the natural universe. Spectrochemical analy-
sis is unsurpassed for the qualitative and quantitative analysis
of minerals, rocks, soils and meteorites. Its advantages in-
clude speed, low cost of analysis, high sensitivity, the provi-
sion of a permanent record of analysis both of the elements
sought and of others which may turn out to be of interest, and
a very wide range of elements which may be detected and esti-
mated.

Rhenium, not discovered until 1925, is properly described
as rare and, hence, unfamiliar. Molybdenites from various parts
of the world are the richest known potential source of rhenium
with concentrations ranging from 0.5 to 1000 ppm. Because of
the recently developed industrial uses, such as fountain pen
points, electrical contact points, electron tube elements, cat-
alysts and electrodeposited protection coatings, rhenium has
become of increasing interest to chemists.

Spectrographic determination of rhenium in molybdenites has
been done with a d.c. arc as the excitation source (12, 29).
With the availability of the plasma jet in the last two years,
it is of interest to apply this new excitation source to the
rhenium determination. Like all other solution techniques, the
plasma jet has the "built-in" advantage of ease of sample and

standard preparation. Good sensitivity and precision is expected from this excitation source.

This research studied the characteristics of the plasma arc with respect to the rhenium determination. Rhenium from various molybdenites and other ores of Utah and Arizona origins was determined by use of the rhenium emission line at 3460.5 A, and the lengthy procedure formerly developed by Ho (29) was simplified as a result of this research. Results of studies on the determination of rhenium with the plasma arc are presented and compared with those using the d.c. arc as well as the thiocyanate colorimetric procedure (55).

SURVEY OF THE LITERATURE

In the past, much work has been done on the chemical determination of rhenium from various ores; in nearly all cases, separation of rhenium from the interfering elements—such as molybdenum, iron, and copper—was found necessary. These separations have been accomplished by means of precipitation, distillation, liquid-liquid extraction, ion-exchange and combinations of two or more of them.

Among the separations by distillation may be listed the method by Geilmann and Weibke (18), which utilizes the technique of passing a stream of moist HCl diluted with CO_2 through a hot concentrated H_2SO_4 solution of the perrhenate, followed by a gravimetric determination of rhenium which collects in the distillate. In another method (19) advanced by these authors the molybdenum is separated by precipitation from nearly neutral

solutions with 8-hydroxyquinoline. Both methods work satis-
factorily for the ranges in which they were intended, but when
applied to the problem of separating five gram lots of molybdic
anhydride from 0.1 mg. or less rhenium are not at all satis-
factory. This same method was used by Zimakov (66) whereby
molybdenum was separated from rhenium by precipitation with
8-hydroxyquinoline and the remaining molybdenum hydroxyquinolate
was extracted with chloroform. Radioactive Mo^{99} and Re^{186} were
used as indicators.

Much the same may be said of the methods of Kronman and his
students (39), as well as the work of Mikhailova, Pevsner, and
Archipova (46) who used a combination of the distillation tech-
nique with the 8-hydroxyquinoline method to effect the deter-
mination. The rhenium generally was determined by a nitron
acetate precipitation. Another distillation method was devel-
oped by Iordanov and Pavlova (33), in which fused rhenium ores
were distilled in concentrated H_2SO_4 with ten per cent HCl
slowly added. The escaping gas was absorbed in NaOH solution
and then was acidified for a thiocyanate photometric determina-
tion. 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.

Yen and Tao (65) used a rapid chemical method for the de-
termination of rhenium in molybdenite. They found that rhenium,
as perrhenate, could be completely coprecipitated with Ph_4AsClO_4
in either neutral, acidic or alkaline solution and the resulting

recovery of rhenium was above 99 per cent.

In an early paper Hurd described a method (31) whereby the molybdenum was extracted from solutions containing rhenium by first treating them with ethyl xanthate, followed by a $CHCl_3$ extraction of the molybdenum complex thus formed. The rhenium was then determined by reaction with $SnCl_2$ and KSCN. Later in 1960, in a paper reported by Cusicanqui and Paredes (8), molybdenite samples were fused with NaOH and Na_2O_2 in a nickel crucible, the fused mass was dissolved in water, the solution neutralized with H_2SO_4 and the molybdenum oxidized with liquid bromine, with care to avoid boiling, because rhenium compounds are volatile in H_2SO_4 solution. The pH was adjusted to 9-11 with NaOH and the molybdenum separated by means of potassium xanthate with HCl and $CHCl_3$. The rhenium remaining in the aqueous phase was reduced with $SnCl_2$ and determined as a furil dioxime complex (25).

Willard and Smith (64) developed a method whereby the per-rhenate could be precipitated from solutions with tetraphenylar-sonium chloride. From the work of these authors, it is apparent that molybdate does not interfere greatly, but unfortunately, it is not possible to precipitate the minute amounts of rhenium which are usually present in molybdenites.

Pillipenko and Obolonchik (53) stated that rhenium in the form of perrhenate formed a complex with methyl violet which could be extracted by benzene or toluene. The presence of 40-fold of molybdenum over rhenium did not hinder the reaction, but a larger amount of molybdenum lowered the sensitivity. Later when Okubo (50) used the same method, he reported that molybdenum

or tungsten less than 200 times the concentration of rhenium would not interfere, but ClO_4^-, phthalate, I^-, SCN^-, NO_3^-, and ClO_3^- would.

Hoffmann and Lundell (30) used a differential reduction with mercury to effect the required separation. Under certain conditions only the molybdate was reduced and was extracted with ether after treatment with thiocyanate. Farayan and Mushegyan (13) also developed a method of separation of rhenium from molybdenum based on the reduction of molybdate in 1 N H_2SO_4 medium. The reduced molybdenum formed a colored compound with KSCN which could be separated with ether.

Malyutina, Dobkina and Chernikhov (43) reported a differential spectrophotometric method, which was based on the thiourea method (60). The rhenium complex with thiourea is more stable than the rhenium thiocyanate complex. This method is applicable to the determination of rhenium in the intermediate products obtained in the manufacture of perrhenates from rhenium containing raw material.

Spectrophotometric determination of rhenium with 4-methylnioxime was used by Kassner, Ting and Grove (36). Interfering elements commonly found in molybdenite concentrate and molybdenite roaster flue dust were removed by three operations: evaporation with HCl, precipitation of hydrous oxides with NH_4OH, and formation of organometallic compounds with ethyl xanthate and $CHCl_3$ extraction. From 0.001 to 1.0 per cent of rhenium could be readily determined. Kenna (37) showed that an orange color developed on treatment of rhenium with dimethylglyoxime

and SnCl₂-HCl solution. The method was applicable for one to
260 ppm of rhenium with an accuracy of five per cent.

A completely satisfactory method for the quantitative de-
termination of rhenium in molybdenite minerals was not developed
until 1940 (28), because of a combination of several analytical
difficulties. First, there is enough chemical similarity be-
tween rhenium and molybdenum to make clear cut separations some-
what difficult. Secondly, although molybdenites contain the
highest natural concentrations of rhenium that have been found,
these concentrations are of the order of 0.0001 to 0.001 per
cent. In addition, no colorimetric reaction for the determina-
tion of rhenium has been developed in which molybdenum does not
interfere. Consequently it becomes 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 developed a method for the quantitative de-
termination (28) of five microgram amounts of rhenium in the
presence of a million-fold excess of molybdenum which combines
a modified distillation and modified colorimetric technique. A
similar method was used by Mubayadzhyan, Nadzharyan and Sarkis-
yan (48) in 1961, in which rhenium was determined by a thio-
cyanate complex after extraction and reextraction with 1-butanol.

Other methods following separation of molybdenum from
rhenium are: first, the colorimetric determination whereby per-
rhenate interacts with diphenylcarbazide in 0.1-8.0 N HCl forming
a violet complex at 430-540 mu (45, 57); second, the photometric
determination whereby perrhenate reacts with diethyldithio-

phosphoric acid in the presence of $SnCl_2$ on heating and the orange compound soluble in C_6H_6 is determined at 436 mu (38); third, the spectrophotometric determination of rhenium using syn-phenyl-2-pyridyl ketoxime (22); and fourth, the photometric determination of rhenium with α-pyridyl dioxime (63). In 1963, Fryer, Calliford and Yardley used α-furil dioxime for the spectrometric determination of up to 600 micrograms of rhenium at 532 mu in the presence of 500 times as much molybdenum (16).

A rapid procedure for the separation of molybdenum and rhenium was described by Prosad and Yatirayam (54). They reduced various amounts of rhenium as perrhenate and molybdenum as molybdate in 8 N HCl with N_2H_4-2HCl by boiling 15 minutes. They extracted molybdenum (III) with amyl acetate in HCl solution, leaving rhenium (IV) in the aqueous phase. The distributions of perrhenate between the aqueous phase and $CHCl_3$ in the presence of organic bases were studied by Navratil and Toul (49). 2,3,5-triphenyltetrazolium chloride was found to be the best for extracting perrhenate. They reported it was possible to separate perrhenate selectively from molybdenum and tungsten; after extraction using $CHCl_3$, perrhenate was re-extracted by ascorbic acid at pH 10.5, 2,3,5-triphenyltetrazolium ion was reduced by the ascorbic acid to formazan which remained in the organic phase, and the liberated perrhenate passed into the aqueous phase. Molybdenum could also be separated from rhenium by extraction of the molybdenum cupferrate with $CHCl_3$ in 2 N HCl solution (24). The distribution coefficient between the two

phases was 200; Mo^{99} was used to check the efficiency.

Peterson, MacDuff and Hovey (52) used a quarternary amine as a selective extractant for rhenium from an alkaline solution. Maeck, Booman, Kussy and Rein (42) studied the distribution of 57 metallic ions for the quarternary amines--tetrapropyl, tetrabutyl and tetrahexyl--into 4-methyl-2-pentanone from five media, HNO_3, H_2SO_4, HF, HCl and NaOH. Many analytical separations seem possible. The separation of rhenium is highly specific except technetium.

Another technique used for the separation of rhenium from molybdenum is ion-exchange chromatography (1, 3, 6, 14, 20, 44, 56). Fischer and Meloche (15) successfully separated mixtures of ReO_4^- and $MoO_4^=$ ions by the use of ion-exchange resins. Their procedure consisted of adsorbing both $MoO_4^=$ and ReO_4^- on Amberlite IRA-400, removing of $MoO_4^=$ selectively with 2.5 N NaOH solution, and finally eluting of the retained ReO_4^- with 7 N HCl. The removal of $MoO_4^=$ by NaOH and ReO_4^- by HCl was time consuming because of the large volume of eluting agents required. Meloche and Preuss (44) improved the procedure for the separation of ReO_4^- from $MoO_4^=$ ions, using Amberlite IRA-400 (ClO_4^-) and thus reduced considerably the volume of eluting agents and the time required. They recommended $K_2C_2O_4$ for the separation and elution of $MoO_4^=$, and $HClO_4$ for the subsequent elution of the ReO_4^- ion.

In 1961, Beyermann (5) developed a colorimetric method to determine traces of rhenium (0.1 to 0.0001 per cent). He sublimed rhenium in an oxygen-air mixture, and then purified it by an Ph_4AsReO_4 extraction. Ph_4AsReO_4 was destroyed via cation-

exchange in Dowex-50 in the H^+ form, and ReO_4^- was determined with fuschin through extraction with amyl acetate. Many ions reacted with fuschin, but the procedure described eliminated most of them. By the addition of $NaNH_4HPO_4$ with fuschin, molybdenum and tungsten were complexed and did not interfere.

In 1962, Ryabchikov, Borison and Gerlit (59) used EDE-10 anion exchanger to separate rhenium from molybdenum and tungsten. They obtained the best results with 25 ml. of a mixture of 0.2 M of H_3PO_4 and 0.6 M of Na_2SO_4. The molybdenum and tungsten were retained on the column with H_2O; molybdenum and tungsten could be eluted with a base. In the same year, Darbinyan and Gabakyan published a series of papers on an ion-exchange method for the separation of rhenium and molybdenum. KU-2 cation exchanger (H^+ form) was used and rhenium was eluted with 0.005 N HCl at 2-4 ml./min., then molybdenum was eluted with one of the following: 2.5 M NH_4OH, 5 per cent NaOH, 6N H_3PO_4 or 2 N HCl (9). It could also be done by adding 10 per cent thiourea to the rhenium and molybdenum solution and passing the solution through a 20 cm. column of KU-2 cation exchanger (H^+ form) at 2-3 ml./ min. The column was washed twice with 10 ml. H_2O, and rhenium was determined in the filtrate by the thiourea method. Separation was almost complete. Oxalic acid or $K_2C_2O_4$ were the best eluents for molybdenum (10). The separation of rhenium from molybdenum and technetium was studied with the AU-18 anion exchanger in various concentrations of HCl and NaOH and in the static and dynamic conditions by these same authors. The maximum relative adsorption of rhenium occurred in 0.5 to 2.0 N acid

and 2.5 to 5.0 N base under static conditions. For the separation of a small amount of rhenium from molybdenum and from small amounts of technetium, the flow rate should be 8 ml./min., and the resin should be in the Cl⁻ form. The best eluent for rhenium was $HClO_4$ (11).

In 1964, Hamaguchi, Kawabuchi and Kuroda (23) developed an anion exchange chromotographic procedure for the separation of rhenium (VII) from molybdenum (VI) and technetium (VII). They first eluted Re (VII) with 0.5 M NH_4SCN-0.5 M HCl, and then removed Mo (VI) by 2.5 M NH_4NO_3. They considered a 0.5 M NaOH-0.5 M NaCl solution preferable to NH_4NO_3 when large amounts of Mo (VI) were present. Tc (VII) was eluted with 4 M HNO_3, which gave a Tc (VII) recovery of about 60 per cent. They were able to separate a microgram to a few milligram quantities of Re (VII) from Mo (VI) in proportions of Re:Mo = 1:500 to 170:1 and from traces of Tc (VII).

Besides gravimetric and photometric determinations, many other methods have been used for the determination of rhenium. Among these are listed the fluorimetric determination of rhenium in ores with Rhodamine 6 Zh and Rhodamine 6G by Ivankava and Shcherbov (34, 35), the titrimetric determination with $SnCl_2$ by Henze and Geyer (26), the radiochemical method with Re^{188} and Re^{186} as indicators by Graf (21), the spectrophotometric catalytic ability of rhenium for the reduction of tellurate by $SnCl_2$ by Simon and Grimaldi (62), the polarographic method by Heyrovsky (27), and finally the spectrographic determinations by Fain (12) and by Ho (29) separately. Fain discussed the

spectrographical determination of rhenium in which rhenium was
discharged from the sample in the first 30-40 seconds by a d.c.
arc at ten amperes. Cadmium was used as the internal standard
and PbO was used as the buffer. When the rhenium 3460.5 A line
was measured the error was 12 per cent, and the maximum sensi-
tivity was 0.00004 per cent. Ho (29) also determined rhenium
spectrographically at 3460.5 A with a d.c. arc as the excitation
source at 12.5 amperes. Cobalt was used as the internal stan-
dard. Preliminary concentration of rhenium was done by the fol-
lowing procedure: samples were placed in solution with HNO_3 and
evaporated to dryness. The residue was taken up in HCl, then
filtered, and the filtrate was evaporated. Excess NH_4OH was
added and the solution filtered. The filtrate was evaporated to
2 ml. Two ml. of a 10 M NaOH and 2 ml. of 0.1 M tetrabutyl am-
monium 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 added as the internal
standard. The precision of this method showed a probable error
of less than five per cent. The average deviation was about ten
per cent below the thiocyanate colorimetrically determined values.

No references have been found in the literature dealing
with the rhenium determination by plasma arc spectroscopy. The
research problem presented here, therefore, was to study the
characteristics of the plasma arc with respect to the rhenium
determination and to simplify the rhenium concentration pro-
cedure proposed by S. C. Ho.

EXPERIMENTAL

Description of Apparatus

The spectrograph used in this research is a large Littrow-mounted quartz spectrograph made by the Bausch and Lomb Optical Company. In a Littrow mount spectrograph the birefringence effect of quartz is eliminated, as a single 30° prism with a reflecting coat of evaporated aluminum on its back surface is employed, so that the rays traverse the prism twice, in opposite directions. It has the additional advantage that only a single quartz lens is needed for both collimating and focusing. The length of the system may be considered as having been folded together in the middle by the use of an autocollimation principle. The dispersion is equivalent to that of an instrument of the ordinary type almost twice as long. The quartz prism and lens are mounted on a carriage that moves along a slide, their positions being determined by means of a scale and index. The prism can be rotated to photograph various regions of the spectrum on a 4 x 10 inch plate. The plate-holder can be tilted to bring it into coincidence with the focal curve for any spectral region between 2100 and 8000 A. In the model used, all necessary adjustments for any spectral region can be carried out from the operator's position at the slit end of the instrument.

The plasma jet used in this research is a model D NSL plasma arc. It consists of a solution plasma assembly, a tangential gas control, a siphon gas control, optical lenses and a water cooling system. The main body of the plasma jet contains the

water cooled graphite anode and cathode electrode assembly, entry ports for the tangential gas supply, and an atomizer control unit. The solution to be analyzed is placed in a small beaker and atomized with the siphon gas into the discharge chamber. An arc plasma formed between the two graphite electrodes is constricted by the magnetodynamic effects and by tangential gas and then is forced through the upper cathode electrode orifice to the tungsten control rod in the form of a flame-like jet at a temperature of about $6000^{\circ}K$. The atomizer used is a modified Beckman medium bore type atomizer. The power supply delivers 19.0 amperes at 300 volts. The plasma arc is placed on the optical bench 13 inches from the slit. The optical system consists of one quartz lens of three inches focal length placed 5.5 inches from the plasma jet.

The illuminating system of the d.c. arc consists of the electrode holders, a spherical condensing lens, and a rotating disk. The samples are excited with a direct current generator of 150 volts and about 12.5 amperes.

Line intensities are obtained by means of an Allied Research Laboratories-Dietert densitometer. The colorimeter used in this research was a Beckman DU spectrophotometer.

Spectrographic Conditions

Table 1. Comparison of d.c. arc and plasma arc excitation
conditions.

	Plasma arc	D.C. arc
Voltage	300 volts	150 volts
Current	19.0 amp.	12.5 amp.
Exposure	60 sec.	40 sec.
Sector	----	3/8 open
Slit width	0.020 mm.	0.020 mm.
Tilt	278	278
Focus	56	56
Tangential gas	helium at 60 liters/min.	----
Siphon gas	argon at 1.4-2.0 liters/min.	----
Sample	approx. 0.5 ml./min.	50 λ solution dried on electrode
Internal standard	cobalt	cobalt
Spectrographic buffer	----	LiCl
Re line used	3460.5 Å	3460.5 Å
Co line used	3453.5 Å	3453.5 Å

Spectrographic Procedure

Electrodes for the d.c. arc were prepared from spectro-
graphic graphite purchased from the National Carbon Company.
The cathode was shaped to a sharp point and the anode was

prepared by drilling a well in one end of the electrode, three
to four millimeters in depth. The anode was ready for use after
being filled with CCl_4 saturated with Carnauba wax followed by
oven drying at $110^{\circ}C$ for 15 minutes. Samples on the waxed anodes
were dried in an air oven at $110^{\circ}C$ overnight.

The solvent chosen for plasma arc analysis was a 50-50 mix-
ture of water and ethanol. The solution to be analyzed was
placed in a five ml. beaker and atomized with the siphon gas
into the discharge chamber.

Eastman Kodak SA-1 plates were selected as the most sensi-
tive plates readily available. After exposure the plates were
developed in Eastman D-19 developer for five minutes at $68^{\circ}F$,
then fixed, washed and dried. Line intensities were determined
with an ARL-Dietert densitometer.

Preliminary Work

The rhenium line at 3460.5 A is satisfactory for quantita-
tive analysis only after the interfering elements have been re-
moved. Table 2 shows the possible interfering lines and their
wavelengths.

Table 2. Possible interfering lines that appear in
the region of the rhenium line at 3460.5 A.

Element	Wavelength, A	Relative line intensity
Rhenium	3460.5	1000$_w$
Chromium	3460.43	40
Copper	3459.43	25
Iron	3459.92	80
Manganese	3460.33	60
Molybdenum	3460.78	25

Therefore, the interfering elements must be separated by some chemical means previous to spectrographic analysis. The principles of extraction suggested by Peterson et al. (52) and Maeck et al. (42) were adopted, and preliminary studies were made on the separation procedure developed by Ho (29). A special effort was made to simplify this method, since it was not only lengthy but also gave a result ten per cent lower than that of the colorimetric determination.

First, work was carried out closely following Ho's procedure:

1. One gram of sample was weighed, treated with 25 ml. of concentrated HNO_3 and evaporated almost to dryness.

2. Then, 20 ml. of concentrated HCl was added to dissolve most of the white precipitate.

3. The solution was filtered and the filtrate evaporated to dryness.

4. Excess NH_4OH was added to the above and the mixture was filtered again.

5. The filtrate above was evaporated to 2 ml., and 2 ml. of 0.1 M tetrabutyl ammonium bromide and 2 ml. of 10 M NaOH were added.

6. Extractions were carried out with four portions of 5 ml. of 4-methyl-2-pentanone.

Since the amounts of molybdenite ores furnished from the U. S. Geological Survey were limited, all preliminary work on sample preparation and extraction efficiency was done on a synthetic ore, a mixture primarily of oxides prepared to simulate

the composition of molybdenite. The spectrographic result obtained after the above concentration procedure was 18 per cent below that of the colorimetric determination as shown in Table 4.

Thus, improvement on the above extraction method was obviously necessary. The final procedure was developed as following:

1. One gram of sample was treated with 10 ml. of concentrated HNO_3 and evaporated to 2 ml.

2. To the above, 15 ml. of concentrated HCl was added; then the solution was evaporated to 2 ml.

3. Fifteen ml. of 10 M NaOH was then added; the precipitate was filtered, washed with a minimum amount of water and was drained.

4. To the filtrate, 3 ml. of 0.1 M tetrabutyl ammonium bromide was added, and the rhenium was extracted with five 10 ml. portions of 4-methyl-2-pentanone.

Because of the appreciable volatility of perrhenate, caution must be taken to keep the temperature below $85^{\circ}C$ (36). It appears that there is no loss of rhenium in HCl or HNO_3 solutions under these conditions (58). All residues and aqueous layers to be discarded were checked spectrographically to see that they were free from rhenium.

Spectrographic determinations were done with both d.c. and plasma arc excitations, and the results showed a maximum deviation of 4.6 per cent from the colorimetrically determined values. Results of the preliminary studies on the synthetic ore are presented later in Tables 4, 5 and 6.

Selection of the Internal Standard

One common practice in quantitative spectrographic analysis is to use an internal standard. The standard may be an element already present in known amount in the specimen, or it may be an extraneous element added in known quantity to all samples. This procedure eliminates errors due to inequalities of plate characteristics and development. It also compensates for variations likely to occur in the d.c. arc during the excitation of the sample.

In plasma arc analysis, one of the major difficulties is the control of flow rate of the sample solution. By the use of an internal standard, the ratio of the radiant power of a given line of the unknown to that of the internal standard is measured, thus is not affected by minor variations in the flow rate.

Several factors must be considered when an internal standard is to be selected. These are listed by Ahrens and Taylor in their book "Spectrochemical Analysis" (2). To summarize, the line to be used as an internal standard should be as close as possible to the unknown in wavelength and also in emission intensity so that non-linearity of the photographic emulsion with respect to these factors will not be a serious source of error.

Cobalt was chosen to be the internal standard. Table 3 shows the similarity of rhenium and cobalt in their excitation potentials, ionization potentials and wavelengths of their emission lines.

Table 3. Comparison of the excitation potentials and ionization potentials of rhenium and cobalt.

	Cobalt	Rhenium
Excitation potential	4.00	3.75
Ionization potential	7.86	7.85
Emission line, A	3453.5	3460.5

Selection of the Spectrographic Buffer for the D.C. Arc

The purpose of the spectrographic buffer is to minimize the variations in transport mechanism from spectrum to spectrum, thus to increase the precision of the analytical data. 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. Lithium chloride was selected for the buffer for the d.c. arc analysis in this laboratory. A series of various concentrations of reagent solutions were added to the final solutions, and it was found that 0.25 M LiCl gave the best buffering effect.

As for the plasma arc, no spectrographic buffer is needed. The plasma jet operates at a temperature of $8000^{\circ}K$ at a direct current of about 20 amperes. Well above the temperature of a normal d.c. arc, this temperature seems to be responsible for reducing matrix effects significantly (48).

SPECTROGRAPHIC ANALYSIS BY D.C. ARC EXCITATION

Preparation of Standards

In order to compensate for any possible error due to con-
centration of techniques, all standards were carried through the
extraction procedure. To 1 ml. of potassium perrhenate solu-
tion, 3 ml. of 0.1 M tetrabutyl ammonium bromide (Eastman Kodak
Label), and 10 ml. of 10 M NaOH were added. The complexed per-
rhenate in a strong basic medium was then extracted with five
10 ml. portions of 4-methyl-2-pentanone, and the extractants
were combined and evaporated to dryness. It was then treated
twice with 1 ml. of concentrated HNO_3. After the solution was
evaporated to dryness the second time, 1 ml. of 0.1 N HCl was
pipetted into the residue; 1 ml. of 125 ppm cobalt and 0.25 M
LiCl was added as the internal standard and spectrographic buf-
fer. A series of standards were made by extracting 1 ml. of each
of the 500, 400, 300, 200, 100, 50 and 25 ppm rhenium solutions
by the procedure described above and adding to each the same
amount of internal standard and buffer. The $CoCl_2 \cdot 6H_2O$ used as
the internal standard was checked spectrographically and found
to be free from rhenium as an impurity. Then 50 λ of the pre-
pared standard was pipetted onto each electrode and the elec-
trodes were dried in an air oven at $110^{\circ}C$ overnight before they
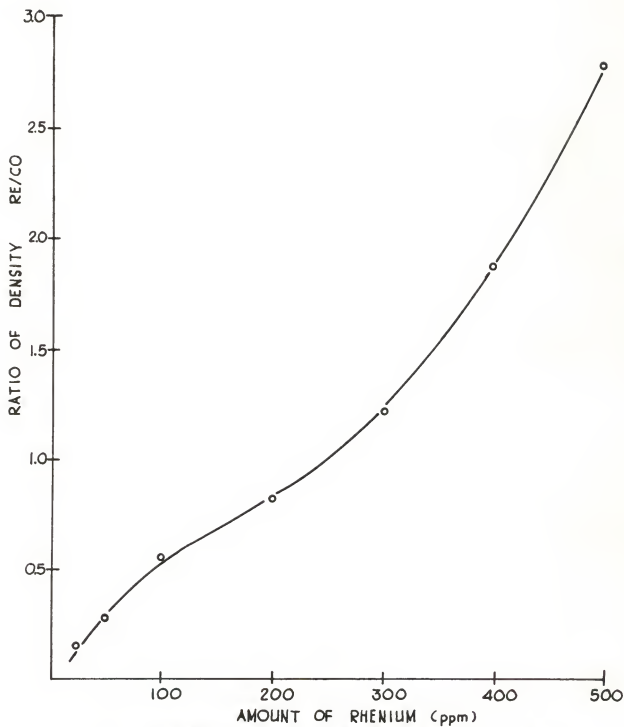were arced. Fig. 1 shows the working curve of rhenium by d.c.
arc excitation.

FIG. 1 WORKING CURVE FOR RHENIUM BY D.C. ARC

Extraction Efficiency and Sample Preparation

First, one gm. of the synthetic rhenium-containing ore was
weighed and carried through the concentration procedure devel-
oped by Ho (29) as described in "Preliminary Work." After evap-
oration of the solvent 4-methyl-2-pentanone, the residue was
treated twice with 1 ml. of concentrated HNO_3. It was then evap-
orated to dryness and taken up in 1 ml. of 0.1 ml. of 0.1N HCl
and 1 ml. of 125 ppm cobalt and 0.25 M LiCl. Fiftyλ of this
solution was then put on each electrode and dried overnight.
The results of the spectrographic determination by d.c. arc
excitation are presented in Table 4.

Since the above results averaged 18 per cent below the
colorimetrically determined value (480 ppm), the concentration
procedure needed to be improved. One gm. of the same synthetic
ore was then treated with 10 ml. of concentrated HNO_3 and evap-
orated to 2 ml. Following this, 15 ml. of concentrated HCl was
added and the solution was evaporated to 2 ml. again. Then 15
ml. of 10 M NaOH was added and the precipitate was filtered off,
washed with a minimum amount of water, and allowed to drain.
Three ml. of 0.1 M tetrabutyl-ammonium bromide was added to the
filtrate and it was then extracted with five 10 ml. portions of
4-methyl-2-pentanone. After the extractant had been evaporated
to dryness, the residue was treated twice with 1 ml. of concen-
trated HNO_3. It was then evaporated to dryness and taken up in
1 ml. of 0.1 N HCl and 1 ml. of 125 ppm cobalt and 0.25 M of
LiCl.

The spectrographic results of the synthetic ore extracted by this modified procedure are presented in Table 5. By use of this modified procedure, the per cent differences between the spectrographic and the colorimetric results averaged 4.6 per cent as compared with 18 per cent using the old procedure. Therefore, the modified concentration procedure was used for all samples throughout this research.

Table 4. Analysis of the synthetic ore extracted by the original procedure to show the precision of the spectrographic method by d.c. arc excitation.

%T Re	%T Co	D_{Re}/Co	ug/gm	Residues $r_i = |x_i - \bar{x}|$	Variances $r_i^2 = (x_i - \bar{x})^2$
8.00	32.00	2.22	442	49	2401
7.75	22.75	1.73	382	11	121
14.00	30.25	1.64	368	25	625
9.25	25.00	1.72	380	13	169
5.00	19.0	1.81	394	1	1
Total			1966		3317
Mean = $\bar{x}$			393		

$$S = \text{Standard deviation} = \sqrt{\frac{\sum r_i^2}{n-1}} = \sqrt{\frac{3317}{5-1}} = 28.8 \text{ ppm}$$

$$S_{\bar{X}} = \text{Standard error} = \frac{S}{\sqrt{n}} = \frac{28.8}{\sqrt{5}} = 12.9 \text{ ppm}$$

$$\text{Probable error} = S_{\bar{X}} \cdot \frac{\sqrt{2}}{2} = (1.29)(0.7) = 9.04 \text{ ppm}$$

$$\text{Per cent standard error} = \frac{12.9}{393} = 3.28\%$$

$$\text{Per cent probable error} = \frac{9.04}{393} = 2.30\%$$

Table 5. Analysis of the synthetic ore extracted by the modified procedure to show the precision of the spectrographic method by d.c. arc excitation.

%T Re	%T Co	$D_{Re/Co}$	ug/gram	Residues $r_i = |x_i - \bar{x}|$	Variances $r_i^2 = (x_i - \bar{x})^2$
18.75	56.50	2.93	520	62	3844
13.75	39.00	2.11	429	29	841
43.75	70.75	2.38	460	2	4
19.00	46.75	2.15	434	24	576
38.50	65.50	2.25	445	13	169
Total			2288		5434
Mean = $\bar{x}$			458		

$$S = \text{Standard deviation} = \sqrt{\frac{\sum r_i^2}{n-1}} = \sqrt{\frac{5434}{4}} = 36.9 \text{ ppm}$$

$$S_{\bar{x}} = \text{Standard error} = \frac{S}{\sqrt{n}} = \frac{36.9}{\sqrt{5}} = 16.5 \text{ ppm}$$

$$\text{Probable error} = S_{\bar{x}} \cdot \frac{\sqrt{2}}{2} = (16.5)(0.7) = 11.4 \text{ ppm}$$

$$\text{Per cent standard error} = \frac{16.5}{458} = 3.62\%$$

$$\text{Per cent probable error} = \frac{11.4}{458} = 2.50\%$$

Precision of D.C. Arc Analysis

The precision of this method was determined by several analyses on the same sample. Averages were obtained and the deviations and probable errors were calculated. Tables 4 and 5 present data which indicate the precision of the method in the analysis of the synthetic rhenium-containing ore extracted by the original and by the simplified procedure respectively. The probable error of the spectrographic determination by the d.c. arc excitation was 2.30 to 2.50 per cent. The mean of the five determinations of the synthetic ore extracted by the simplified procedure was 458 ppm, and the colorimetrically determined value was 460 ppm; the per cent difference was 4.6 per cent.

SPECTROGRAPHIC ANALYSIS BY PLASMA ARC EXCITATION

Preparation of Standards

One ml. of each of the 500, 400, 300, 200, 100, 50, and 25 ppm rhenium standards (made from $KReO_4$) was carried through the extraction procedure as described for preparation of standards for d.c. arc analysis, except that the final solution was made in a 50-50 mixture of water and ethanol. After the extracted rhenium complex in 4-methyl-2-pentanone was evaporated to dryness, it was treated twice with HNO_3 and evaporated to dryness. The residue was taken up in 1 ml. of 0.1 N HCl (in 50 per cent ethanol), and 1 ml. of 200 ppm cobalt (in 50 per cent ethanol) was added as the internal standard. This 50 per cent ethanol solution then was ready for plasma arc determination. Fig. 2
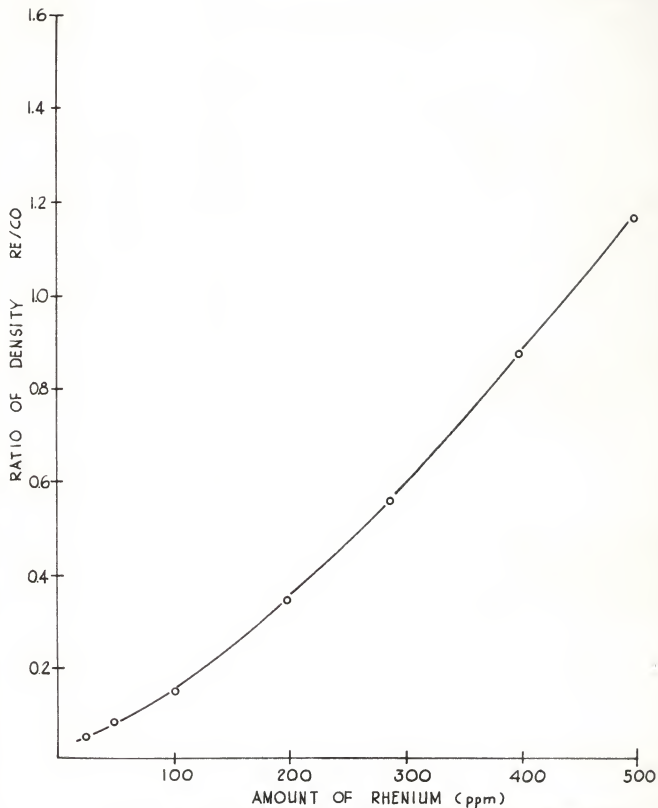
FIG. 2 WORKING CURVE FOR RHENIUM BY PLASMA ARC

shows the working curve of rhenium by plasma arc excitation.

Preparation of Sample Solutions

A certain number of rhenium samples were weighed--0.5 gm. of the synthetic ore; 0.25 gm., 0.5 gm. and 1.0 gm. of the high, medium and low level molybdenites respectively; 1 gm. of MO-1, the molybdic sulfide sample in which rhenium is present as an impurity. The weighed samples were treated with 10 ml. of concentrated HNO_3 and the solution evaporated to 2 ml. Following this, 15 ml. of concentrated HCl was added and the solution was evaporated to 2 ml. again. Then 15 ml. of 10 M NaOH was added and the precipitates, as hydroxides, were filtered off, washed with a minimum amount of water and allowed to drain. Three ml. of 0.1 M tetrabutyl ammonium bromide was added to the filtrate and it was then extracted with five 10 ml. portions of 4-methyl-2-pentanone. After the extractant was evaporated to dryness, the residue was treated twice with 1 ml. of concentrated HNO_3. It was then evaporated to dryness and taken up in 1 ml. of 0.1 N HCl (in 50 per cent ethanol), and 1 ml. of 200 ppm cobalt (in 50 per cent ethanol) was added as the internal standard. Results of plasma arc analysis are presented in Tables 6, 7, 8, 9, and 10.

Table 6. Analysis of the synthetic ore to show the precision
of the spectrographic method by plasma arc excitation.

%T Re	%T Co	D_{Re}/Co	ug/gram	Residues $r_i = \lvert x_i - \bar{x} \rvert$	Variances $r_i^2 = (x_i - \bar{x})^2$
51.50	22.25	0.442	490	10	100
70.75	46.25	0.450	496	16	256
75.75	51.50	0.419	468	12	144
59.00	30.25	0.440	486	6	36
50.00	18.50	0.411	462	18	324
Total			2402		860
Mean = $\bar{x}$			480		

S = Standard deviation = $\sqrt{\dfrac{\sum r_i^2}{n-1}}$ = $\sqrt{\dfrac{860}{4}}$ = 14.7 ppm

$S_{\bar{x}}$ = Standard error = $\dfrac{S}{\sqrt{n}}$ = $\dfrac{14.7}{\sqrt{5}}$ = 6.56 ppm

Probable error = $S_{\bar{x}} \cdot \dfrac{\sqrt{2}}{2}$ = (6.56)(0.7) = 4.60 ppm

Per cent standard error = $\dfrac{6.56}{480}$ = 1.37%

Per cent probable error = $\dfrac{4.60}{480}$ = 0.96%

Table 7. Analysis of molybdenite (high level of rhenium) to show the precision of the spectrographic method by plasma arc excitation.

$\%T$ Re	$\%T$ Co	D_{Re}/Co	$ug/gram$	Residues $r_i = |x_i - \bar{x}|$	Variances $r_i^2 = (x_i - \bar{x})^2$
80.00	60.00	0.436	968	27	729
81.75	61.75	0.418	936	5	25
82.75	63.00	0.409	920	21	441
Total			2824		1195
Mean = $\bar{x}$			941		

$$S = \text{Standard deviation} = \sqrt{\frac{\sum r_i^2}{n-1}} = \sqrt{\frac{1195}{2}} = 24.5 \text{ ppm}$$

$$S_{\bar{x}} = \text{Standard error} = \frac{S}{\sqrt{n}} = \frac{24.5}{\sqrt{3}} = 14.1 \text{ ppm}$$

$$\text{Probable error} = S_{\bar{x}} \cdot \frac{\sqrt{2}}{2} = (14.1)(0.7) = 9.90 \text{ ppm}$$

$$\text{Per cent standard error} = \frac{14.1}{941} = 1.50\%$$

$$\text{Per cent probable error} = \frac{9.90}{941} = 1.05\%$$

Table 8. Analysis of molybdenite (medium level of rhenium) to show the precision of the spectrographic method by plasma arc excitation.

%T Re	%T Co	D_{Re}/C_o	ug/gram	Residues $r_i = |x_i - \bar{x}|$	Variances $r_i^2 = (x_i - \bar{x})^2$
86.50	69.75	0.402	456	2	4
86.00	68.50	0.398	451	3	9
88.75	73.50	0.388	443	11	121
82.25	63.00	0.421	472	18	324
83.25	62.75	0.393	447	7	49
Total			2269		507
Mean = $\bar{x}$			454		

$$S = \text{Standard deviation} = \sqrt{\frac{\sum r_i^2}{n-1}} = \sqrt{\frac{507}{4}} = 11.2 \text{ ppm}$$

$$S_{\bar{x}} = \text{Standard error} = \frac{S}{\sqrt{n}} = \frac{11.2}{\sqrt{5}} = 5.00 \text{ ppm}$$

$$\text{Probable error} = S_{\bar{x}} \cdot \frac{\sqrt{2}}{2} = (5.0)(0.70) = 3.50 \text{ ppm}$$

$$\text{Per cent standard error} = \frac{5.00}{454} = 1.10\%$$

$$\text{Per cent probable error} = \frac{3.50}{454} = 0.78\%$$

Table 9. Analysis of molybdenite (low level of rhenium) to show the precision of the spectrographic method by plasma arc excitation.

%T Re	%T Co	D_{Re}/C_o	ug/gram	Residues $r_i = |x_i - \bar{x}|$	Variances $r_i^2 = (x_i - \bar{x})^2$
88.00	79.00	0.541	285	6	36
88.50	79.75	0.541	285	6	36
87.50	79.25	0.574	297	6	36
86.00	76.50	0.549	288	3	9
79.75	68.00	0.586	302	11	121
Total			1457		208
Mean = $\bar{x}$			291		

$$S = \text{Standard deviation} = \sqrt{\frac{\sum r_i^2}{n-1}} = \sqrt{\frac{208}{4}} = 7.23 \text{ ppm}$$

$$S_{\bar{x}} = \text{Standard error} = \frac{S}{\sqrt{n}} = \frac{7.23}{\sqrt{5}} = 3.22 \text{ ppm}$$

$$\text{Probable error} = S_{\bar{x}} \cdot \frac{\sqrt{2}}{2} = (3.22)(0.7) = 2.25 \text{ ppm}$$

$$\text{Per cent standard error} = \frac{3.22}{291} = 1.11\%$$

$$\text{Per cent probable error} = \frac{2.25}{291} = 0.77\%$$

Table 10. Analysis of rhenium in MO-1 sample to show the precision of the spectrographic method by plasma arc excitation.

%T Re	%T Co	D_{Re}/Co	ug/gram	Residues $r_i = |x_i - \bar{x}|$	Variances $r_i^2 = (x_i - \bar{x})^2$
88.00	64.00	0.286	177	10	100
88.75	63.00	0.258	163	4	16
90.00	66.25	0.256	162	5	25
89.00	62.50	0.247	157	10	100
87.00	61.00	0.281	174	7	49
Total			833		290
Mean = $\bar{x}$			167		

$$S = \text{Standard deviation} = \sqrt{\frac{\sum r_i^2}{n-1}} = \sqrt{\frac{290}{4}} = 8.56 \text{ ppm}$$

$$S_{\bar{x}} = \text{Standard error} = \frac{S}{\sqrt{n}} = \frac{8.56}{\sqrt{5}} = 3.82 \text{ ppm}$$

$$\text{Probable error} = S_{\bar{x}} \cdot \frac{\sqrt{2}}{2} = (3.82)(0.7) = 2.67 \text{ ppm}$$

$$\text{Per cent standard error} = \frac{3.82}{167} = 2.28\%$$

$$\text{Per cent probable error} = \frac{2.67}{167} = 1.60\%$$

Method of Standard Addition

In order to verify the results already obtained, the method of standard addition 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 11 to 16 show the results obtained by adding a definite amount of potassium perrhenate solution to each sample. Because of the limited amounts of MO-2 and MO-3 samples furnished by the U. S. Geological Survey, these two samples were analyzed by the standard addition method only.

Table 11. Analysis of molybdenite (high level rhenium) to show
the precision of the spectrographic standard addition
method by plasma arc excitation.

%T Re	%T Co	D_{Re}/C_{O}	ug/gram obtained	ug/gram added	ug/gram true	Residues $r_i = \|x_i - \bar{x}\|$	Variances $r_i^2 = (x_i - \bar{x})^2$
73.00	54.75	0.523	1112	200	912	30	900
79.50	66.50	0.560	1168	200	968	26	676
81.00	67.00	0.526	1116	200	916	26	676
70.50	52.50	0.542	1140	200	940	2	4
71.50	55.25	0.566	1176	200	976	34	1156
Total					4712		
Mean = $\bar{x}$					942		

$$S = \text{Standard deviation} = \sqrt{\frac{\sum r_i^2}{n-1}} = \sqrt{\frac{3412}{4}} = 29.2 \text{ ppm}$$

$$S_{\bar{x}} = \text{Standard error} = \frac{S}{\sqrt{n}} = \frac{29.2}{\sqrt{5}} = 13.0 \text{ ppm}$$

$$\text{Probable error} = S_{\bar{x}} \cdot \frac{\sqrt{2}}{2} = (13.0)(0.7) = 9.10 \text{ ppm}$$

$$\text{Per cent standard error} = \frac{13.0}{942} = 1.38\%$$

$$\text{Per cent probable error} = \frac{9.10}{942} = 0.97\%$$

Table 12. Analysis of molybdenite (medium level rhenium) to show the precision of the spectrographic standard addition method by plasma arc excitation.

%T Re	%T Co	D_{Re}/Co	ug/gram obtained	ug/gram added	ug/gram true	Residues $r_i = \|x_i - \bar{x}\|$	Variances $r_i^2 = (x_i - \bar{x})^2$
82.75	70.75	0.545	574	100	474	10	100
88.00	79.00	0.541	570	100	470	6	36
90.00	82.00	0.531	564	100	464	0	0
90.00	81.75	0.523	554	100	454	10	100
86.00	75.25	0.525	556	100	456	8	64
Total					2318		300
Mean = $\bar{x}$					464		

S = Standard deviation = $\sqrt{\dfrac{\Sigma r_i^2}{n-1}}$ = $\sqrt{\dfrac{300}{4}}$ = 8.67 ppm

$S_{\bar{x}}$ = Standard error = $\dfrac{S}{\sqrt{n}}$ = $\dfrac{8.67}{\sqrt{5}}$ = 3.87 ppm

Probable error = $S_{\bar{x}} \cdot \dfrac{\sqrt{2}}{2}$ = (3.87)(0.70) = 2.71 ppm

Per cent standard error = $\dfrac{3.87}{464}$ = 0.84%

Per cent probable error = $\dfrac{2.71}{464}$ = 0.58%

Table 13. Analysis of molybdenite (low level rhenium) to show the precision of the spectrographic standard addition method by plasma arc excitation.

%T Re	%T Co	D_{Re}/Co	ug/gram obtained	ug/gram added	ug/gram true	Residues $r_i=|x_i-\bar{x}|$	Variances $r_i^2=(x_i-\bar{x})^2$
42.00	30.00	0.720	698	400	298	2	4
43.00	30.50	0.710	692	400	292	4	16
55.00	44.00	0.728	706	400	306	10	100
64.50	54.50	0.724	702	400	302	6	36
53.50	41.00	0.701	684	400	284	12	144
Total					1482		300
Mean = $\bar{x}$					296		

$$S = \text{Standard deviation} = \sqrt{\frac{\sum r_i^2}{n-1}} = \sqrt{\frac{300}{4}} = 8.67 \text{ ppm}$$

$$S_{\bar{x}} = \text{Standard error} = \frac{S}{\sqrt{n}} = \frac{8.67}{\sqrt{5}} = 3.87 \text{ ppm}$$

$$\text{Probable error} = S_{\bar{x}} \cdot \frac{\sqrt{2}}{2} = (3.87)(0.7) = 2.71 \text{ ppm}$$

$$\text{Per cent standard error} = \frac{3.87}{296} = 1.31\%$$

$$\text{Per cent probable error} = \frac{2.71}{296} = 0.92\%$$

Table 14. Analysis of rhenium in MO-1 sample to show the precision of the spectrographic standard addition method by plasma arc excitation.

%T Re	%T Co	D_{Re}/C_o	ug/gram obtained	ug/gram added	ug/gram true	Residues $r_1 = \lvert x_1 - \bar{x} \rvert$	Variances $r_1^2 = (x_1 - \bar{x})^2$
63.00	44.00	0.563	588	400	188	10	100
75.00	59.00	0.545	572	400	172	6	36
66.50	47.00	0.540	568	400	168	10	100
69.75	52.25	0.555	580	400	180	2	4
68.00	50.25	0.560	584	400	184	6	36
Total					892		276
Mean = $\bar{x}$					178		

$$S = \text{Standard deviation} = \sqrt{\frac{\Sigma r_1^2}{n-1}} = \sqrt{\frac{276}{4}} = 8.32 \text{ ppm}$$

$$S_{\bar{x}} = \text{Standard error} = \frac{S}{\sqrt{n}} = \frac{8.32}{\sqrt{5}} = 3.71 \text{ ppm}$$

$$\text{Probable error} = S_{\bar{x}} \cdot \frac{\sqrt{2}}{2} = (3.71)(0.70) = 2.60 \text{ ppm}$$

$$\text{Per cent standard error} = \frac{3.71}{178} = 2.08\%$$

$$\text{Per cent probable error} = \frac{2.60}{178} = 1.46\%$$

Table 15. Analysis of rhenium in MO-2 sample to show the precision of the spectrographic standard addition method by plasma arc excitation.

%T Re	%T Co	D_{Re}/C_o	ug/gram obtained	ug/gram added	ug/gram true	Residues $r_i = |x_i - \bar{x}|$	Variances $r_i^2 = (x_i - \bar{x})^2$
73.00	48.00	0.429	478	400	78	5	25
76.00	53.00	0.434	482	400	82	1	1
73.50	50.25	0.446	490	400	90	7	49
81.50	62.25	0.430	480	400	80	3	9
79.25	58.50	0.435	484	400	84	1	1
Total					414		85
Mean = $\bar{x}$					83		

$$S = \text{Standard deviation} = \sqrt{\frac{\sum r_i^2}{n-1}} = \sqrt{\frac{85}{4}} = 4.61 \text{ ppm}$$

$$S_{\bar{x}} = \text{Standard error} = \frac{S}{\sqrt{n}} = \frac{4.61}{\sqrt{5}} = 2.06 \text{ ppm}$$

$$\text{Probable error} = S_{\bar{x}} \cdot \frac{\sqrt{2}}{2} = (2.06)(0.70) = 1.44 \text{ ppm}$$

$$\text{Per cent standard error} = \frac{2.06}{83} = 2.48\%$$

$$\text{Per cent probable error} = \frac{1.44}{83} = 1.73\%$$

Table 16. Analysis of rhenium in MO-3 sample to show the precision of the spectrographic standard addition method by plasma arc excitation.

%T Re	%T Co	D_{Re}/Co	ug/gram obtained	ug/gram added	ug/gram true	Residues $r_i=\|x_i-\bar{x}\|$	Variances $r_i^2=(x_i-\bar{x})^2$
45.00	21.50	0.520	552	400	152	2	4
50.25	26.00	0.518	550	400	150	4	16
70.00	51.00	0.530	560	400	160	6	36
Total					462		56
Mean = $\bar{x}$					154		

$$S = \text{Standard deviation} = \sqrt{\frac{\Sigma r_i^2}{n-1}} = \sqrt{\frac{56}{2}} = 5.29 \text{ ppm}$$

$$S_{\bar{x}} = \text{Standard error} = \frac{S}{\sqrt{n}} = \frac{5.29}{\sqrt{3}} = 3.06 \text{ ppm}$$

$$\text{Probable error} = S_{\bar{x}} \cdot \frac{\sqrt{2}}{2} = (3.06)(0.70) = 2.14 \text{ ppm}$$

$$\text{Per cent standard error} = \frac{3.06}{154} = 1.98\%$$

$$\text{Per cent probable error} = \frac{2.14}{154} = 1.39\%$$

Colorimetric Extraction Procedure
Followed by Plasma Arc Determination

In order to verify the validity of the extraction procedure developed in this research, a combination method was devised. One-half gm. of the synthetic ore was weighed and carried through the separation procedure as described on page 42 under the heading of "Thiocyanate Chemical Method." After the removal of molybdenum as molybdenum cupferrate with $CHCl_3$, the aqueous phase was evaporated to dryness. It was then taken up in 1 ml. of 0.1 N HCl (in 50 per cent ethanol), and 1 ml. of 200 ppm cobalt (in 50 per cent ethanol) was added as the internal standard. Table 17 presents the results of the plasma arc analysis of rhenium in the synthetic ore extracted by the colorimetric extracting procedure. This gives an average of 472 ppm, as compared to the previously determined value 480 ppm shown in Table 6. According to the colorimetric determination, the synthetic ore has a rhenium concentration of 480 ppm.

Precision, Accuracy and Sensitivity

The precision of the method was determined by several analyses on the same sample. Tables 6 through 17 present data which indicate the precision of the method in the analyses of seven rhenium containing samples. The probable errors of the spectrographic determinations using the plasma arc as the excitation source range from 0.58 to 1.73 per cent. It is of interest to compare this precision with that of the d.c. arc, 2.30-2.50 per cent, as indicated in Tables 4 and 5.

Table 17. Analysis of the synthetic ore extracted by the colorimetric extracting procedure to show the precision of the spectrographic method by plasma arc excitation.

%T Re	%T Co	D_{Re}/Co	ug/gram	Residues $r_i = |x_i - \bar{x}|$	Variances $r_i^2 = (x_i - \bar{x})^2$
88.5	50.5	.179	480	8	64
86.25	43.0	.174	464	8	64
77.75	24.0	.177	472	0	0
Total			1416		128
Mean = $\bar{x}$			472		

$$S = \text{Standard deviation} = \sqrt{\frac{\sum r_i^2}{n-1}} = \sqrt{\frac{128}{2}} = 8.0 \text{ ppm}$$

$$S_{\bar{x}} = \text{Standard error} = \frac{S}{\sqrt{n}} = \frac{8.0}{\sqrt{3}} = 4.61 \text{ ppm}$$

$$\text{Probable error} = S_{\bar{x}} \cdot \frac{2}{2} = (4.61)(0.7) = 3.23 \text{ ppm}$$

$$\text{Per cent standard error} = \frac{4.61}{472} = 0.98\%$$

$$\text{Per cent probable error} = \frac{3.23}{472} = 0.69\%$$

The accuracy of this method was determined by comparison of the averages with the chemically determined values. Per cent differences are presented in Table 18. Maximum difference between the methods is four per cent.

Sensitivity depends on various factors among which may be listed the optical system, the size of the atomizer, the exposure time, and the flow rate of the siphon gas. In this research, maximum sensitivity with respect to rhenium solutions was found to be 12.5 ppm at a siphon flow rate of 2.0 liters per minute and an exposure time of 60 seconds.

COMPARISON OF SPECTROGRAPHIC ANALYSIS AND THIOCYANATE CHEMICAL METHOD

Before a spectrographic procedure can be accepted with confidence, it must undergo a favorable comparison with a well-known chemical method. The method chosen for comparison was the widely used thiocyanate colorimetric procedure (55).

A certain amount of sample was weighed and dissolved in 10 ml. of concentrated HNO_3. The solution was evaporated to 2 ml., 15 ml. of concentrated HCl was added, and the evaporation was repeated. The HCl evaporation was repeated three times in order to remove nitric acid, since the presence of NO_3^- interferes with the thiocyanate color formation. 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.

Following this, 15 ml. of amyl alcohol was added and the solution was shaken vigorously. The extractions of the aqueous layer were repeated a second and a third time, using 10 ml. quantities of amyl alcohol, and the extractants were combined 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 stannous chloride dissolved in the amyl alcohol. The amyl alcohol solution was then evaporated carefully to a volume of about 2 ml., which was then allowed to cool; about 1 ml. of concentrated HNO_3 was cautiously added. After the initial vigorous reaction had subsided, another 5 ml. of HNO_3 was added, the solution was gently heated in order to complete the oxidation. Ten ml. of concentrated HCl was then added, and the solution was evaporated to 2 ml. This process was repeated three times to remove the nitric acid. The solution was then diluted with 25 ml. of water and enough cupferron (about 2 gm.) in 10 ml. of water was added to complete the precipitation. The mixture was then filtered, the precipitate being allowed to drain. The filtrate was extracted within an hour (24) with three successive 20 ml. portions of $CHCl_3$; 10 ml. of HCl was then added, the solution was again extracted twice with 20 ml. portions of $CHCl_3$. Six ml. of KCNS and 2 ml. of $SnCl_2$ (in 6N HCl) solution were added to the aqueous layer, which was then shaken and extracted with 20 ml. of amyl alcohol. The orange-yellow color in the amyl alcohol was measured with a Beckman DU Spectrophotometer at a wavelength of 430 mu.
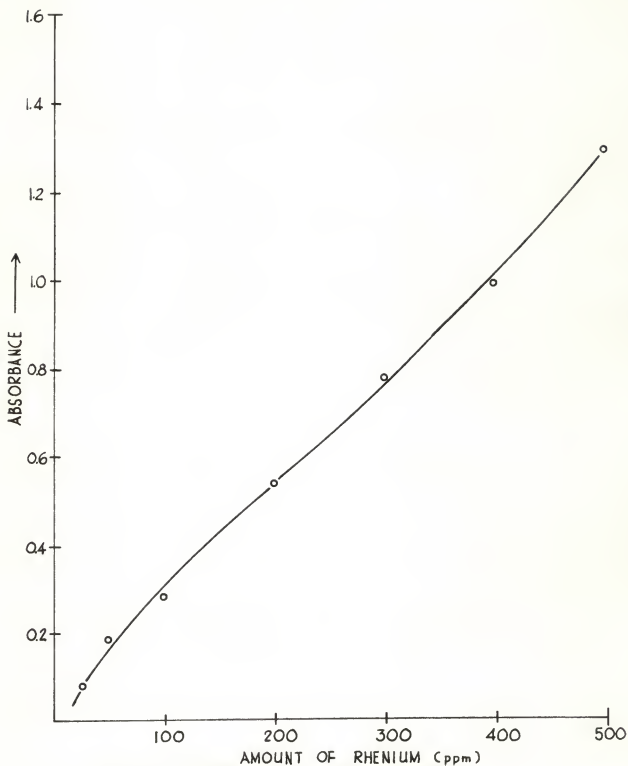
The concentration of rhenium was determined by comparison

FIG. 3 COLORIMETRIC WORKING CURVE

Table 18. Comparison of spectrographic and thiocyanate methods of analyses of seven rhenium samples.

Sample	Thiocyanate ppm	D.C. arc spectrographic	Plasma arc spectrographic ppm	Difference ppm	Difference per cent
High level molybdenite					
Regular procedure	950	--	941	9	-0.95%
Standard addition	--	--	942	8	-0.85%
Medium level molybdenite					
Regular procedure	452	--	454	2	+0.44%
Standard addition	--	--	464	12	+2.65%
Low level molybdenite					
Regular procedure	292	--	291	1	-0.34%
Standard addition	--	--	296	4	1.37%
MO-1 (MoS2)					
Regular procedure	174	--	167	7	-4.01%
Standard addition	--	--	178	4	2.30%
MO-2 (MoO2)					
Regular procedure	86	--	--	--	---
Standard addition	--	--	83	3	-3.49%
MO-3 (MoO2)					
Regular procedure	159	--	--	--	---
Standard addition	--	--	154	5	-3.15%
Synthetic ore					
Regular procedure	480	--	480	0	0%
Standard addition	--	--	--	--	---
D.C. arc	--	458	--	22	-4.60%
After extraction of Re by colorimetric extracting procedure	--	--	472	8	-1.67%

with the standard curve shown in Fig. 3. Standard solutions
were prepared by pipetting 0.5 ml. of each of the 500, 400, 300,
200, 100, 50, and 25 ppm rhenium solutions (made from $KReO_4$),
adding to each 6 ml. of 20 per cent KCNS solution and 2 ml. of
25 per cent of $SnCl_2$ (in 6 N HCl), and extracting each with 20
ml. of amyl alcohol.

CONCLUSIONS

A plasma arc spectrographic procedure of good precision for
the determination of rhenium has been developed. The separation
of rhenium from its interfering elements was made by the extrac-
tion of rhenium tetrabutyl ammonium complex with 4-methyl-2-
pentanone in a strong basic medium. The extraction procedure
previously developed by Ho (29) was modified, whereby the treat-
ment with ammonium hydroxide was omitted, and the accuracy of
this simplified method improved by a factor of four when using
the colorimetrically determined values as references.

The solvent chosen was a 50-50 mixture of water and ethanol.
Cobalt was selected as the internal standard. Helium and argon
were used as the tangential and siphon gases respectively.

The minimum concentration that still gave a readable line
was 12.5 ppm of rhenium. The precision of this method showed an
average probable error less than 1.5 per cent. The values com-
pared satisfactorily with those of the thiocyanate chemical pro-
cedure. The average difference between these two methods was
1.77 per cent.

ACKNOWLEDGMENT

LITERATURE CITED

(1) Aanliz, R.
Separation of molybdenum from rhenium by the ion exchange chromatographic method. Tsvetnykh Metal. i Producktiv ikh Pererabotki, 12:89. 1956.

(2) Ahrens, L. H.
Spectrochemical Analysis. Mass.: Addison-Wesley Press, 1950.

(3) Ana, Lopez Emanuelli.
The behavior of molybdates and perrhenates in ion exchange resins. Anales fac. quim. Y farm, 10:113. 1958.

(4) Arefeva, T., A. Pozdnyakova, and R. Pats.
Determination of rhenium in the presence of molybdenum in rhenium concentrates. Referat. Zhur., Met. No. 3421. 1957.

(5) Beyermann, Klaus.
Colorimetric determination of traces of rhenium. Z. Anal. Chem., 183: 91. 1961.

(6) Blaedel, W., and N. D. Olsen.
Sequential ion exchange separation scheme for the identification of metallic radioelements. Anal. Chem., 32: 1866. 1958.

(7) Brode, W.
Chemical Spectroscopy. New York: John Wiley and Sons, 1939.

(8) Cusicanqui, H., and E. Paredes.
Determination of rhenium in molybdenite. Fac. Cienc. Fis Mat., Anales, 17: 133. 1960.

(9) Darbinyan, M., and D. Gaibakyan.
Ion-exchange separation of rhenium and molybdenum I. Izv. Akad. Nauk Arm. SSR. Khim. Nauki, 15: 217. 1962.

(10) Darbinyan, M., and D. Gaibakyan.
Ion-exchange separation of rhenium and molybdenum II. Izv. Akad. Nauk Arm. SSR. Khim. Nauki, 15: 321. 1962.

(11) Darbinyan, M., and D. Gaibakyan.
Ion-exchange separation of rhenium and molybdenum III. Izv. Akad. Nauk Arm. SSR. Khim. Nauki, 15: 511. 1962.

(12) Fain, E. E.
Spectrographic analysis of rhenium and osmium in ores. Vestn. Akad. Nauk Kaz. SSR., 19: 53. 1963.

(13) Farayan, V., and L. G. Mushegyan.
New method of separation of rhenium from molybdenum.
Doklady Akad. Nauk. Armyan. SSR., 27: 157. 1958.

(14) Faris, J. P.
Adsorption of the elements from hydrofluoric acid by
anion exchange. Ana. Chem., 32: 520. 1960.

(15) Fisher, S., and V. Meloche.
Separation of perrhenate and molybdate ions by use of
ion exchange resins. Anal. Chem., 24: 1100. 1952.

(16) Fryer, F., D. Galliford, and T. Yardley.
The analytical behavior of purified α-furil dioxime with
particular reference to the determination of rhenium in
the presence of molybdenum. Analyst, 88: 191. 1963.

(17) Geilmann, W.
Colorimetric determination of rhenium. Z. anorg. allgem.
Chem., 208: 217. 1932.

(18) Geilmann, W., and F. Weibke.
Separation of molybdenum and rhenium by the method of
distillation. Z. anorg. allgem. Chem., 199: 120. 1931.

(19) Geilmann, W., and F. Weibke.
Separation of molybdenum and rhenium with 8-hydroxy-
quinoline. Z. anorg. allgem. Chem., 199: 347. 1931.

(20) Ginsburg, L., and E. P. Shkrobot.
Separation of molybdenum and rhenium by ion exchange
chromatography. Sbornik Nauch. Trudov Gosudarst Nauch-
Issledovatel Inst. Tsventnoi Met., No. 12: 89. 1956.

(21) Graf, Guenter.
Rhenium extraction with radioactive-isotope indicator.
Freiberger Forschunsh, B64: 91. 1962.

(22) Guyon, C., and Murmann, R. K.
Spectrophotometric determination of rhenium using syn-
phenyl-2-pyridyl ketoxime. Anal. Chem., 36: 1058. 1964.

(23) Hemaguchi, H., K. Kawabuchi, and R. Kuroda.
Anion exchange separation of rhenium from molybdenum and
technetium in thiocyanate chloride media. Anal. Chem.,
36(8): 1654. 1964.

(24) Healy, W., and W. McCabe.
Extraction of submicrogram amounts of molybdenum with
cupferron-CHCl$_3$ using Mo^{99}. Anal. Chem., 35(13): 2117.
1963.

(25) Heaney, R., and E. Malouf.
      Rhenium papers symp., Chicago, 200-270. 1960.

(26) Henze, G., and R. Geyer.
      Volumetric determination of rhenium with stannous chlo-
      ride solution and oxidation-reduction indicator. Z. Anal.
      Chem., 200: 434. 1964.

(27) Heyrovsky, J.
      A sensitive polarographic test for the absence of thenium
      in manganese. Nature, 135: 870. 1935.

(28) Hiskey, C., and V. W. Meloche.
      Determination of rhenium in molybdenite minerals. Ind.
      Eng. Chem., Anal. Ed., 12: 503. 1940.

(29) Ho, Show-ji.
      Spectrographic determination of rhenium in molybdenite
      with the d.c. arc. A Master's Thesis. Dept. of Chem.,
      Kansas State University. 1964.

(30) Hoffmann, J., and G. Lundell.
      Separation of rhenium from molybdenum by the differential
      reduction method with mercury. J. Research Natl. Bur.
      Stds., 23: 497. 1939.

(31) Hurd, L. C.
      Separation of molybdenum and rhenium by the method of
      extraction with ethyl xanthate. Ind. Eng. Chem., Anal.
      Ed., 8: 11. 1936.

(32) Hurd, L. C., and C. F. Hiskey.
      Determination of rhenium in pyrolusite. Ind. Eng. Chem.,
      Anal. Ed., 10: 623. 1938.

(33) Iordanov, N., and M. Pavlova.
      Separation of rhenium by distillation. Mikrochim. Icho-
      anal Acta., 3: 477. 1963.

(34) Ivankova, A., and D. Scherbov.
      Determination of rhenium in mineral ores with Rhodamine
      6G. Metody Analiza Khim. Reaklivov i Preparatov, Gos
      Kom. Sov. Min. SSR. po Khim., No. 4: 107. 1962.

(35) Ivankova, A., and D. Shcherbov.
      Fluorimetric determination of rhenium in ores with
      Rhodamine 6Zh. Zavodsk. Lab., 29(7): 787. 1963.

(36) Kassner, J., S. Ting, and E. Grove.
      Spectrophotometric determination of rhenium with 4-methyl-
      nioxime. Talanta, 7: 269. 1961.

(37) Kenna, B. T.
    Spectrophotometric determination. Anal. Chem., 33: 1130.
    1961.

(38) Kolthoff, I., and P. J. Elving.
    Treatise on Analytical Chemistry. Part II(7). New York:
    Interscience Publishers. 503-532. 1961.

(39) Kronman, E., and V. Bibikova.
    Separation of molybdenum and rhenium by the combination
    of distillation and 8-hydroxyquinoline. J. Applied Chem.
    USSR, 7: 47. 1934.

(40) Lagarev, A., and V. Rodsaevskii.
    Photometric determination of rhenium with diethyldithio-
    phosphoric acid. Zhur. Anal. Khim., 16: 243. 1963.

(41) Langstroth, G., and D. McRae.
    Transport of material in sources for spectroscopic
    analysis. Canad. J. Res., 16A: 61. 1938.

(42) Maeck, W., G. Booman, M. Kussy, and J. Rein.
    Extraction of the elements as the quaternary amine com-
    plexes. Anal. Chem., 33: 1775. 1961.

(43) Malyutina, T., B. Dobkina, and Y. Chernikhov.
    Determination of rhenium by the differential spectro-
    photometric method. Zavodskaya Lab., 26: 259. 1960.

(44) Meloche, V., and A. Preuss.
    Analytical separation of rhenium and molybdenum by ion
    exchange. Anal. Chem., 26: 1911. 1954.

(45) Meshri, D., and B. Haldar.
    Spectrophotometric determination of rhenium with diphenyl-
    carbazide. Indian J. Chem., 1(8): 334. 1963.

(46) Mikhailova, C., D. Pevsner, and N. Archipova.
    Separation of molybdenum and rhenium. Z. Anal. Chem.,
    91: 25. 1932.

(47) Mitteldorf, A., and D. O. Landon.
    The stabilized plasma jet analyzer. The Spex Speaker,
    8(1). 1963.

(48) Mubayadzhyan, M., S. Nadsharyan, and A. Sarkisyan.
    A new method of thiocyanate determination for rhenium
    after extraction and reextraction with butanol. Nauchn.
    Tr., Nauchn.-Issled. Corn.-Met. Inst., Sov. Nar. Khoz.
    Arm. SSR., 2: 267. 1961.

(49) Navratil, O., and J. Toul.
      Extraction of perrhenate by 2,3,5-triphenyltetrazolium
      chloride in CCl_4. Collection Czech. Chem. Commn., 28:
      1848. 1963.

(50) Okubo, Teiji.
      Photometric determination of rhenium with methyl violet.
      Bunseki Kagaku, 12: 937. 1963.

(51) Pakhomova, K., and L. Volkova.
      Polarographic determination of microgram amounts of
      rhenium. Zavodskaya Lab., 25: 1291. 1959.

(52) Peterson, H., J. MacDuff, and M. Hovey.
      Isolation and colorimetric determination of rhenium.
      U. S. Bur. Mines, Rept. Invest. No. 5889: 32. 1961.

(53) Pilipenko, A., and V. A. Obolonchik.
      Reaction of rhenium with methyl violet. Dopovidi Akad.
      Nauk. Ukr. R.S.R., No. 6: 648. 1958.

(54) Prodad, R., and V. Yatirajam.
      Separation of rhenium and molybdenum by extraction with
      amyl acetate. Indian J. Chem. 2(6): 249. 1964.

(55) Rodden, Clement.
      Analytical Chemistry of the Manhattan Project. New York:
      McGraw-Hill. 1950.

(56) Ryabchikov, D., and L. V. Borisova.
      Adsorption of molybdenum and rhenium from various media
      on anionite EDE-10 and chromatographic parting of these
      elements. Zhru. Anal. Khim, 13: 155. 1958.

(57) Ryabchikov, D., and L. V. Borisova.
      Interaction of perrhenate with diphenylcarbazide and
      diphenylcarbozone. Zh. Analit. Khem., 18(7): 851. 1963.

(58) Ryabchikov, D., and L. V. Borisova.
      New spectrophotometric methods for the determination
      of rhenium. Talanta, 10: 13. 1963.

(59) Ryabchikov, D., L. V. Borisova, and B. Gerlit.
      Chromatographic separation of rhenium from molybdenum
      and tungsten with mixed eluents on EDE-10 anion ex-
      changer. Analit. Khim., 17: 890. 1962.

(60) Ryabchikov, D., and A. Lazarev.
      Colorimetric determination of rhenium. Zhur. Anal. Khim.
      10: 4228. 1955.

(61) Sandell, E. B.
      Colorimetric determination of Traces of Metals. 2nd Ed.
      New York: Interscience, 511-522. 1950.

(62) Simon, F., and F. Grimaldi.
      Spectrophotometric catalytic determination of small
      amounts of rhenium in mineralized rocks and molybdenite.
      Anal. Chem. 34: 1361. 1962.

(63) Trussel, F., and R. Thompson.
      Spectrophotometric determination of rhenium with α-pyridil
      dioxime. Anal. Chem. 16(9): 1870. 1964.

(64) Willard, H. H., and G. M. Smith.
      Determination of rhenium by the precipitation with tetra-
      phenylarsonium chloride. Ind. Eng. Chem., Anal. Ed. 11:
      305. 1939.

(65) Yen, J. Y., and T. N. Tao.
      Separation of rhenium by coprecipitation and its deter-
      mination in molybdenite. Hua Hsueh Hsueh Pao, 24: 97.
      1958.

(66) Zimakov, I. E.
      Radioactive indicator for control of separation of rhenium
      and molybdenum. Sb. Nauchn. Tr., Gos. Nauchn.-Issled.
      Inst. Tsvetn. Metal., No. 18: 56. 1961.

PLASMA ARC EXCITATION FOR THE SPECTROGRAPHIC
DETERMINATION OF RHENIUM

by

COLETTE WEN-LI CHANG

B. S., Mount Saint Scholastica College, 1963

———————————

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1965

Spectrographic determination of rhenium was done recently through the use of a d.c. arc. With the availability of the plasma arc in the last two years, it is of interest to apply this new excitation source for the determination of rhenium. This research was carried out to study the behavior of the plasma arc with respect to rhenium and to evaluate the usefulness of plasma arc spectroscopy for the determination of rhenium containing ores.

Since rhenium is one of the extremely rare elements, quantitative determination of rhenium from natural sources is complicated, due both to its low concentration and to the presence of interfering elements. Therefore, it was found necessary to first concentrate rhenium. Ho reported in her thesis (29) a concentration procedure by successive extractions with 4-methyl-2-pentanone. Since it not only was lengthy but also gave results ten per cent lower than those from the thiocyanate chemical method, further investigations of the extraction procedure were carried out in this research. The following procedure was much simpler and gave results within two per cent of the colorimetrically determined values.

Samples were placed in solution with concentrated HNO_3 and evaporated to about two ml. The residue was taken up in concentrated HCl and evaporated again to about two ml. An excess of 10 M NaOH was then added and the solution was filtered. To the filtrate two ml. of 0.1 M tetrabutyl ammonium bromide was added. Separation of rhenium as the tetrabutyl ammonium complex was accomplished through five successive extractions with

4-methyl-2-pentanone. The extracts were then evaporated to
dryness and taken up in 0.1 N HCl in 50 per cent ethanol. Co-
balt was added as the internal standard.

The spectrograph used was a Bausch and Lomb large Littrow
with quartz optics. A Model D NSL plasma arc was used. Helium
and argon were selected as the tangential and siphon gases re-
spectively. The samples were excited at a d.c. potential of
300 volts and a current of 19.0 amperes. Spectra were recorded
on Eastman Kodak SA-1 plates and developed in D-19 developer.
Line densities were determined with an ARL-Dietert densitometer.
The rhenium line at 3460.5 A was used for analytical purposes
with the cobalt line at 3453.5 A as the internal standard.

Seven samples, including three molybdenites were deter-
mined in the course of this study. The ores contained 941, 454,
291, 167, 83, 154, and 480 ppm of rhenium respectively. These
compared satisfactorily with those obtained by the use of a
colorimetric method. The standard addition method used indi-
cated a complete recovery of rhenium. The precision of the
method was determined by a series of analyses of each sample.
The spectrographic precision showed an average probable error
of less than 1.5 per cent. The maximum sensitivity achieved
was 12.5 ppm of rhenium solution at a sample aspiration rate of
0.5 ml. per minute.