PLASMA ARC EXCITATION FOR THE SPECTROGRAPHIC DETERMINATION OF RHENIUM

by

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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 analysis is unsurpassed for the qualitative and quantitative analysis of minerals, rocks, soils and meteorites. Its advantages include speed, low cost of analysis, high sensitivity, the provision 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 estimated.

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, catalysts 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 CO₂ through a hot concentrated H₂SO₄ 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 satisfactorily 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 satisfactory. 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 technique with the 8-hydroxyquinoline method to effect the determination. The rhenium generally was determined by a nitron acetate precipitation. Another distillation method was developed by Iordanov and Pavlova (33), in which fused rhenium ores were distilled in concentrated H$_2$SO$_4$ with ten per cent HCl slowly added. The escaping gas was absorbed in NaOH solution and then was acidified for a thiocyanate photometric determination. 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 determination of rhenium in molybdenite. They found that rhenium, as perrhenate, could be completely coprecipitated with Ph$_4$AsClO$_4$ 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 CHCl₃ extraction of the molybdenum complex thus formed. The rhenium was then determined by reaction with SnCl₂ and KSCN. Later in 1960, in a paper reported by Cusicanqui and Paredes (8), molybdenite samples were fused with NaOH and Na₂O₂ in a nickel crucible; the fused mass was dissolved in water, the solution neutralized with H₂SO₄ and the molybdenum oxidized with liquid bromine, with care to avoid boiling, because rhenium compounds are volatile in H₂SO₄ solution. The pH was adjusted to 9-11 with NaOH and the molybdenum separated by means of potassium xanthate with HCl and CHCl₃. The rhenium remaining in the aqueous phase was reduced with SnCl₂ 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 bensene 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 ClO₄⁻, phthalate, I⁻, SCN⁻, NO₃⁻, and ClO₃⁻ 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 H₂SO₄ medium. The reduced molybdenum formed a colored compound with KSCN which could be separated with ether.

Malyutina, Dobkina and Chernikho (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 NH₄OH, and formation of organometallic compounds with ethyl xanthate and CHCl₃ 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 determination 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 between rhenium and molybdenum to make clear cut separations somewhat 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 determination 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 determination (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 Mubayadzhiyan, Nadzharyan and Sarkisyan (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 perrhenate interacts with diphenylcarbazide in 0.1-3.0 N HCl forming a violet complex at 430-540 με (45, 57); second, the photometric determination whereby perrhenate reacts with diethylldithio-
phosphoric acid in the presence of SnCl₂ on heating and the orange compound soluble in C₆H₆ is determined at 436 μm (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 μm 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 N₂H₄·2HCl 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 CHCl₃ in the presence of organic bases were studied by Navratil and Toul (49). 2,3,5-triphenyltetrasiloxonium 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 CHCl₃, perrhenate was re-extracted by ascorbic acid at pH 10.5, 2,3,5-triphenyltetrasiloxonium 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 CHCl₃ 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. Meeck, Booman, Kussy and Rein (42) studied the distribution of 57 metallic ions for the quarternary amines—tetrapropyl, tetra-butyl and tetrahexyl—into 4-methyl-2-pentanone from five media, HNO$_3$, H$_2$SO$_4$, 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$_4^{2-}$ ions by the use of ion-exchange resins. Their procedure consisted of adsorbing both MoO$_4^{2-}$ and ReO$_4^-$ on Amberlite IRA-400, removing of MoO$_4^{2-}$ selectively with 2.5 N NaOH solution, and finally eluting of the retained ReO$_4^-$ with 7 N HCl. The removal of MoO$_4^{2-}$ 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$_4^{2-}$ ions, using Amberlite IRA-400 (ClO$_4^-$) and thus reduced considerably the volume of eluting agents and the time required. They recommended K$_2$C$_2$O$_4$ for the separation and elution of MoO$_4^{2-}$, and HClO$_4$ for the subsequent elution of the ReO$_4^-$ ion.

In 1961, Bayermann (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$_4$AsReO$_4$ extraction. Ph$_4$AsReO$_4$ was destroyed via cation-
exchange in Dowex-50 in the \( H^+ \) form, and \( \text{ReO}_4^- \) 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 \( \text{NaNH}_4\text{HPO}_4 \) 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 \( \text{H}_3\text{PO}_4 \) and 0.6 M of \( \text{Na}_2\text{SO}_4 \). The molybdenum and tungsten were retained on the column with \( \text{H}_2\text{O} \); 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 M HCl at 2-4 ml./min., then molybdenum was eluted with one of the following: 2.5 M \( \text{NH}_4\text{OH} \), 5 per cent \( \text{NaOH} \), 6N \( \text{H}_3\text{PO}_4 \) or 2 M 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. \( \text{H}_2\text{O} \), and rhenium was determined in the filtrate by the thiourea method. Separation was almost complete. Oxalic acid or \( \text{K}_2\text{C}_2\text{O}_4 \) 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 \( \text{NaOH} \) 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 chromatographic procedure for the separation of rhenium (VII) from molybdenum (VI) and technetium (VII). They first eluted Re (VII) with 0.5 M NH\(_4\)SCN-0.5 M HCl, and then removed Mo (VI) by 2.5 M NH\(_4\)NO\(_3\). They considered a 0.5 M NaOH-0.5 M NaCl solution preferable to NH\(_4\)NO\(_3\) 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 sensitivity was 0.00004 per cent. Ho (29) also determined rhenium spectrographically at 3460.5 Å with a d.c. arc as the excitation source at 12.5 amperes. Cobalt was used as the internal standard. Preliminary concentration of rhenium was done by the following procedure: samples were placed in solution with HNO₃ and evaporated to dryness. The residue was taken up in HCl, then filtered, and the filtrate was evaporated. Excess NH₄OH 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 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 M 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 procedure 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 8000°C. 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.**

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

**Spectrographic Procedure**

Electrodes for the d.c. arc were prepared from spectrographic 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 \( \text{CCl}_4 \) saturated with Carinauba wax followed by oven drying at 110°C for 15 minutes. Samples on the waxed anodes were dried in an air oven at 110°C overnight.

The solvent chosen for plasma arc analysis was a 50-50 mixture 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 sensitive plates readily available. After exposure the plates were developed in Eastman D-19 developer for five minutes at 68°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 quantitative analysis only after the interfering elements have been removed. 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* |
| 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 Maack 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 HNO₃ 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 NH₄OH 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 HNO₃ 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°C (36). It appears that there is no loss of rhenium in HCl or HNO₃ solutions under these conditions (38). 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.

<table>
<thead>
<tr>
<th></th>
<th>Cobalt</th>
<th>Rhenium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excitation potential</td>
<td>4.00</td>
<td>3.75</td>
</tr>
<tr>
<td>Ionization potential</td>
<td>7.86</td>
<td>7.85</td>
</tr>
<tr>
<td>Emission line, A</td>
<td>3453.5</td>
<td>3460.5</td>
</tr>
</tbody>
</table>

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 concentration of techniques, all standards were carried through the extraction procedure. To 1 ml. of potassium perrhenate solution, 3 ml. of 0.1 M tetrabutyl ammonium bromide (Eastman Kodak Label), and 10 ml. of 10 M NaOH were added. The complexed perrhenate 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 HNO₃. After the solution was evaporated to dryness the second time, 1 ml. of 0.1 M 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 buffer. 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 CoCl₂·6H₂O used as the internal standard was checked spectrographically and found to be free from rhenium as an impurity. Then 50 ml of the prepared standard was pipetted onto each electrode and the electrodes were dried in an air oven at 110°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 developed by Ho (29) as described in "Preliminary Work." After evaporation of the solvent 4-methyl-2-pentanone, the residue was treated twice with 1 ml. of concentrated HNO₃. It was then evaporated to dryness and taken up in 1 ml. of 0.1 M HCl and 1 ml. of 125 ppm cobalt and 0.25 M LiCl. Fifty A 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 HNO₃ and 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 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 concentrated HNO₃. It was then evaporated to dryness and taken up in 1 ml. of 0.1 M 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.

<table>
<thead>
<tr>
<th>Re</th>
<th>Co</th>
<th>D_{Re/Co}</th>
<th>ug/gm</th>
<th>Residues</th>
<th>Variances</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.00</td>
<td>32.00</td>
<td>2.22</td>
<td>442</td>
<td>49</td>
<td>2401</td>
</tr>
<tr>
<td>7.75</td>
<td>22.75</td>
<td>1.73</td>
<td>382</td>
<td>11</td>
<td>121</td>
</tr>
<tr>
<td>14.00</td>
<td>30.25</td>
<td>1.64</td>
<td>368</td>
<td>25</td>
<td>625</td>
</tr>
<tr>
<td>9.25</td>
<td>25.00</td>
<td>1.72</td>
<td>380</td>
<td>13</td>
<td>169</td>
</tr>
<tr>
<td>5.00</td>
<td>19.0</td>
<td>1.81</td>
<td>394</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>1966</td>
<td></td>
<td>3317</td>
</tr>
<tr>
<td>Mean = X</td>
<td></td>
<td></td>
<td>393</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

\[ S_X = \text{Standard error} = \frac{S}{\sqrt{n}} = \frac{28.8}{\sqrt{5}} = 12.9 \text{ ppm} \]

Probable error = \( S_X \cdot \frac{\sqrt{2}}{2} = (1.29)(0.7) = 9.04 \text{ ppm} \)

Per cent standard error = \( \frac{12.9}{393} = 3.28\% \)

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.

<table>
<thead>
<tr>
<th>%T Re</th>
<th>%T Co</th>
<th>D_{Re/Co}</th>
<th>μg/gram</th>
<th>Residues</th>
<th>Variances $r_i^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.75</td>
<td>56.50</td>
<td>2.93</td>
<td>520</td>
<td>62</td>
<td>3844</td>
</tr>
<tr>
<td>13.75</td>
<td>39.00</td>
<td>2.11</td>
<td>429</td>
<td>29</td>
<td>841</td>
</tr>
<tr>
<td>43.75</td>
<td>70.75</td>
<td>2.36</td>
<td>460</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>19.00</td>
<td>46.75</td>
<td>2.15</td>
<td>434</td>
<td>24</td>
<td>576</td>
</tr>
<tr>
<td>38.50</td>
<td>65.50</td>
<td>2.25</td>
<td>445</td>
<td>13</td>
<td>169</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>2288</td>
<td></td>
<td>5434</td>
</tr>
<tr>
<td>Mean = $\bar{x}$</td>
<td></td>
<td></td>
<td>458</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

\[ S_x = \text{Standard error} = \frac{S}{\sqrt{n}} = \frac{36.9}{\sqrt{5}} = 16.5 \text{ ppm} \]

\[ \text{Probable error} = S_x \cdot \frac{\sqrt{2}}{2} = (16.5)(0.7) = 11.4 \text{ ppm} \]

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

\[ \text{Per cent probable error} = \frac{11.4}{458} = 2.50\% \]
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 HNO₃ 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 HNO₃. It was then evaporated to dryness and taken up in 1 ml. of 0.1 M 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.

<table>
<thead>
<tr>
<th>%T Re</th>
<th>%T Co</th>
<th>D_{Re/Co}</th>
<th>μg/gram</th>
<th>Residues</th>
<th>Variances</th>
</tr>
</thead>
<tbody>
<tr>
<td>51.50</td>
<td>22.25</td>
<td>0.442</td>
<td>490</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>70.75</td>
<td>46.25</td>
<td>0.450</td>
<td>496</td>
<td>16</td>
<td>256</td>
</tr>
<tr>
<td>75.75</td>
<td>51.50</td>
<td>0.419</td>
<td>468</td>
<td>12</td>
<td>144</td>
</tr>
<tr>
<td>59.00</td>
<td>30.25</td>
<td>0.440</td>
<td>486</td>
<td>6</td>
<td>36</td>
</tr>
<tr>
<td>50.00</td>
<td>18.50</td>
<td>0.411</td>
<td>462</td>
<td>18</td>
<td>324</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>2402</td>
<td>860</td>
<td></td>
</tr>
</tbody>
</table>

Mean = \bar{X} = 480

S = \text{Standard deviation} = \sqrt{\frac{\sum r_1^2}{n-1}} = \sqrt{\frac{360}{4}} = 14.7 \text{ ppm}

S_{\bar{X}} = \text{Standard error} = \frac{S}{\sqrt{n}} = \frac{14.7}{\sqrt{5}} = 6.56 \text{ ppm}

\text{Probable error} = S_{\bar{X}} \cdot \frac{\sqrt{2}}{2} = (6.56)(0.7) = 4.60 \text{ ppm}

\text{Per cent standard error} = \frac{6.56}{480} = 1.37\%

\text{Per cent probable error} = \frac{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     |                                   |                                  |

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

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

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

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

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.

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

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

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

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

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

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.

<table>
<thead>
<tr>
<th>%T Re</th>
<th>%T Co</th>
<th>D_{Re/Co}</th>
<th>µg/gram</th>
<th>Residues</th>
<th>Variances</th>
</tr>
</thead>
<tbody>
<tr>
<td>88.00</td>
<td>79.00</td>
<td>0.541</td>
<td>285</td>
<td>6</td>
<td>36</td>
</tr>
<tr>
<td>88.50</td>
<td>79.75</td>
<td>0.541</td>
<td>285</td>
<td>6</td>
<td>36</td>
</tr>
<tr>
<td>87.50</td>
<td>79.25</td>
<td>0.574</td>
<td>297</td>
<td>6</td>
<td>36</td>
</tr>
<tr>
<td>86.00</td>
<td>76.50</td>
<td>0.549</td>
<td>288</td>
<td>3</td>
<td>9</td>
</tr>
<tr>
<td>79.75</td>
<td>68.00</td>
<td>0.586</td>
<td>302</td>
<td>11</td>
<td>121</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>1457</td>
<td></td>
<td>208</td>
</tr>
<tr>
<td>Mean = \bar{x}</td>
<td></td>
<td></td>
<td>291</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ S = \sqrt{\frac{\sum r_i^2}{n-1}} = \sqrt{\frac{208}{4}} = 7.23 \text{ ppm} \]

\[ S_x = \sqrt{\frac{S^2}{n}} = \sqrt{\frac{7.23^2}{5}} = 3.22 \text{ ppm} \]

Probable error = \[ S_x \cdot \sqrt{\frac{2}{2}} = (3.22)(0.7) = 2.25 \text{ ppm} \]

Per cent standard error = \[ \frac{3.22}{291} = 1.11\% \]

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.

<table>
<thead>
<tr>
<th>%T Re</th>
<th>%T Co</th>
<th>D_re/Co</th>
<th>ug/gram</th>
<th>Residues</th>
<th>Variances</th>
</tr>
</thead>
<tbody>
<tr>
<td>88.00</td>
<td>64.00</td>
<td>0.286</td>
<td>177</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>88.75</td>
<td>63.00</td>
<td>0.258</td>
<td>163</td>
<td>4</td>
<td>16</td>
</tr>
<tr>
<td>90.00</td>
<td>66.25</td>
<td>0.256</td>
<td>162</td>
<td>5</td>
<td>25</td>
</tr>
<tr>
<td>89.00</td>
<td>62.50</td>
<td>0.247</td>
<td>157</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>87.00</td>
<td>61.00</td>
<td>0.281</td>
<td>174</td>
<td>7</td>
<td>49</td>
</tr>
<tr>
<td>Total</td>
<td>833</td>
<td></td>
<td>290</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean = \bar{X}</td>
<td>167</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

\[ S_{\bar{X}} = \text{Standard error} = \frac{S}{\sqrt{n}} = \frac{8.56}{\sqrt{5}} = 3.82 \text{ ppm} \]

\[ \text{Probable error} = S_{\bar{X}} \cdot \frac{\sqrt{2}}{2} = (3.82)(0.7) = 2.67 \text{ ppm} \]

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

\[ \text{Per cent probable error} = \frac{2.67}{167} = 1.60\% \]
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.

<table>
<thead>
<tr>
<th>%T</th>
<th>%T</th>
<th>Re/Co: ug/gram</th>
<th>ug/gram</th>
<th>Residues</th>
<th>Variances</th>
</tr>
</thead>
<tbody>
<tr>
<td>73.00</td>
<td>54.75</td>
<td>0.523</td>
<td>1112</td>
<td>200</td>
<td>912</td>
</tr>
<tr>
<td>79.50</td>
<td>66.50</td>
<td>0.560</td>
<td>1168</td>
<td>200</td>
<td>968</td>
</tr>
<tr>
<td>81.00</td>
<td>67.00</td>
<td>0.526</td>
<td>1116</td>
<td>200</td>
<td>916</td>
</tr>
<tr>
<td>70.50</td>
<td>52.50</td>
<td>0.542</td>
<td>1140</td>
<td>200</td>
<td>940</td>
</tr>
<tr>
<td>71.50</td>
<td>55.25</td>
<td>0.566</td>
<td>1176</td>
<td>200</td>
<td>976</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean = ( \bar{x} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

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

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

Per cent standard error = \( \frac{13.0}{942} = 1.38\% \)

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.

<table>
<thead>
<tr>
<th>%T</th>
<th>%T</th>
<th>Re/Co: ug/gram</th>
<th>Re/Co: ug/gram: obtained</th>
<th>true</th>
<th>Residues</th>
<th>Variances</th>
</tr>
</thead>
<tbody>
<tr>
<td>82.75</td>
<td>70.75</td>
<td>0.545</td>
<td>574</td>
<td>100</td>
<td>474</td>
<td>10</td>
</tr>
<tr>
<td>88.00</td>
<td>79.00</td>
<td>0.541</td>
<td>570</td>
<td>100</td>
<td>470</td>
<td>6</td>
</tr>
<tr>
<td>90.00</td>
<td>82.00</td>
<td>0.531</td>
<td>564</td>
<td>100</td>
<td>464</td>
<td>0</td>
</tr>
<tr>
<td>90.00</td>
<td>81.75</td>
<td>0.523</td>
<td>554</td>
<td>100</td>
<td>454</td>
<td>10</td>
</tr>
<tr>
<td>86.00</td>
<td>75.25</td>
<td>0.525</td>
<td>556</td>
<td>100</td>
<td>456</td>
<td>8</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2318</td>
<td></td>
</tr>
<tr>
<td>Mean = X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>464</td>
<td></td>
</tr>
</tbody>
</table>

\[ S = \text{Standard deviation} = \sqrt{\frac{\sum r_i^2}{n-1}} = \sqrt{\frac{300}{9}} = 8.67 \text{ ppm} \]

\[ S_x = \text{Standard error} = \frac{S}{\sqrt{n}} = \frac{8.67}{\sqrt{5}} = 3.87 \text{ ppm} \]

\[ \text{Probable error} = S_x \cdot \frac{2}{2} = (3.87)(0.70) = 2.71 \text{ ppm} \]

\[ \text{Per cent standard error} = \frac{3.87}{464} = 0.84\% \]

\[ \text{Per cent probable error} = \frac{2.71}{464} = 0.58\% \]
Table 13. Analysis of molybdenite (low level rhenium) to show the precision of the spectrographic standard addition method by plasma arc excitation.

| %T | %T | \( \frac{\text{Re}}{\text{Co}} \) ug/gram | ug/gram obtained | true | Residues | Variances \( r_1 = |x_1 - \bar{x}|^2 \) |
|----|----|-----------------|----------------|------|----------|----------------|
| 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 = \( \bar{x} \)

\[ S = \text{Standard deviation} = \sqrt{\frac{\sum r_1^2}{n-1}} = \sqrt{\frac{300}{4}} = 8.67 \text{ ppm} \]

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

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

Per cent standard error = \( \frac{3.87}{296} = 1.31\% \)

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.

<table>
<thead>
<tr>
<th>%T</th>
<th>%T</th>
<th>Re/Co</th>
<th>ug/gram</th>
<th>ug/gram</th>
<th>ug/gram</th>
<th>Residues</th>
<th>Variances</th>
</tr>
</thead>
<tbody>
<tr>
<td>63.00</td>
<td>44.00</td>
<td>0.563</td>
<td>588</td>
<td>400</td>
<td>188</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>75.00</td>
<td>59.00</td>
<td>0.545</td>
<td>572</td>
<td>400</td>
<td>172</td>
<td>6</td>
<td>36</td>
</tr>
<tr>
<td>66.50</td>
<td>47.00</td>
<td>0.540</td>
<td>568</td>
<td>400</td>
<td>168</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>69.75</td>
<td>52.25</td>
<td>0.555</td>
<td>580</td>
<td>400</td>
<td>180</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>68.00</td>
<td>50.25</td>
<td>0.560</td>
<td>584</td>
<td>400</td>
<td>184</td>
<td>6</td>
<td>36</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>892</td>
<td></td>
<td>276</td>
</tr>
</tbody>
</table>

Mean = \( \bar{x} \)

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

\[
S_x = \text{Standard error} = \frac{S}{\sqrt{n}} = \frac{8.32}{\sqrt{5}} = 3.71 \text{ ppm}
\]

Probable error = \( S_x \cdot \frac{r_2}{2} = (3.71)(0.70) = 2.60 \text{ ppm} \)

Per cent standard error = \( \frac{3.71}{178} = 2.08\% \)

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.

<table>
<thead>
<tr>
<th>%T:</th>
<th>%T:</th>
<th>Re/Co:</th>
<th>ug/gram:</th>
<th>ug/gram:</th>
<th>Residues:</th>
<th>Variances:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Re:</td>
<td>Co:</td>
<td>obtained:</td>
<td>added:</td>
<td>true:</td>
</tr>
<tr>
<td>73.00</td>
<td>48.00</td>
<td>0.429</td>
<td>478</td>
<td>400</td>
<td>78</td>
<td>5</td>
</tr>
<tr>
<td>76.00</td>
<td>53.00</td>
<td>0.434</td>
<td>482</td>
<td>400</td>
<td>82</td>
<td>1</td>
</tr>
<tr>
<td>73.50</td>
<td>50.25</td>
<td>0.446</td>
<td>490</td>
<td>400</td>
<td>90</td>
<td>7</td>
</tr>
<tr>
<td>81.50</td>
<td>62.25</td>
<td>0.430</td>
<td>480</td>
<td>400</td>
<td>80</td>
<td>3</td>
</tr>
<tr>
<td>79.25</td>
<td>58.50</td>
<td>0.435</td>
<td>484</td>
<td>400</td>
<td>84</td>
<td>1</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>414</td>
<td></td>
</tr>
<tr>
<td>Mean = \bar{x}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>83</td>
<td></td>
</tr>
</tbody>
</table>

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

S_x = Standard error = \frac{S}{\sqrt{n}} = \frac{4.61}{\sqrt{5}} = 2.06 ppm

Probable error = S_x \cdot \frac{\sqrt{2}}{2} = (2.06)(0.70) = 1.44 ppm

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

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.

<table>
<thead>
<tr>
<th>%T :</th>
<th>%T :</th>
<th>D Re/Co: ug/gram</th>
<th>ug/gram</th>
<th>ug/gram:</th>
<th>Residues</th>
<th>Variances</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re</td>
<td>Co</td>
<td>obtained</td>
<td>added</td>
<td>true</td>
<td>r₁ =</td>
<td>r₁ = (x₁ - x)^2</td>
</tr>
<tr>
<td>45.00</td>
<td>21.50</td>
<td>0.520</td>
<td>552</td>
<td>400</td>
<td>152</td>
<td>2</td>
</tr>
<tr>
<td>50.25</td>
<td>26.00</td>
<td>0.518</td>
<td>550</td>
<td>400</td>
<td>150</td>
<td>4</td>
</tr>
<tr>
<td>70.00</td>
<td>51.00</td>
<td>0.530</td>
<td>560</td>
<td>400</td>
<td>160</td>
<td>6</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>462</td>
<td></td>
</tr>
<tr>
<td>Mean = ( \bar{x} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>154</td>
<td></td>
</tr>
</tbody>
</table>

\[ S = \text{Standard deviation} = \sqrt{\frac{\sum r_1^2}{n-1}} = \sqrt{\frac{56}{2}} = 5.29 \text{ ppm} \]

\[ S_x = \text{Standard error} = \frac{S}{\sqrt{n}} = \frac{5.29}{\sqrt{3}} = 3.06 \text{ ppm} \]

\[ \text{Probable error} = S_x \cdot \frac{\sqrt{2}}{2} = (3.06)(0.70) = 2.14 \text{ ppm} \]

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

\[ \text{Per cent probable error} = \frac{2.14}{154} = 1.39\% \]
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 CHCl₃, 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.

<table>
<thead>
<tr>
<th>%T Re</th>
<th>%T Co</th>
<th>ΔR̂e/Co</th>
<th>ug/gram</th>
<th>Residues</th>
<th>Variances</th>
</tr>
</thead>
<tbody>
<tr>
<td>88.5</td>
<td>50.5</td>
<td>.179</td>
<td>4.80</td>
<td>3</td>
<td>64</td>
</tr>
<tr>
<td>86.25</td>
<td>43.0</td>
<td>.174</td>
<td>4.64</td>
<td>8</td>
<td>64</td>
</tr>
<tr>
<td>77.75</td>
<td>24.0</td>
<td>.177</td>
<td>4.72</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>14.16</td>
<td>128</td>
<td></td>
</tr>
<tr>
<td>Mean = \overline{x}</td>
<td></td>
<td></td>
<td>4.72</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

\[
S_\overline{x} = \text{Standard error} = \frac{S}{\sqrt{n}} = \frac{8.0}{\sqrt{3}} = 4.61 \text{ ppm}
\]

Probable error = \[ S_\overline{x} \cdot \sqrt{\frac{2}{2}} = (4.61)(0.7) = 3.23 \text{ ppm}\]

Per cent standard error = \[ \frac{4.61}{4.72} = 0.98\% \]

Per cent probable error = \[ \frac{3.23}{4.72} = 0.69\% \]
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 HNO₃. 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 NO₃⁻ 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 SnCl₂ (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 HNO₃ was cautiously added. After the initial vigorous reaction had subsided, another 5 ml. of HNO₃ 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 CHCl₃; 10 ml. of HCl was then added, the solution was again extracted twice with 20 ml. portions of CHCl₃. Six ml. of KCNS and 2 ml. of SnCl₂ (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 nm.

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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thiocyanate ppm</th>
<th>D.C. arc spectrographic</th>
<th>Plasma arc spectrographic</th>
<th>Difference ppm</th>
<th>Difference per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>High level molybdenite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Regular procedure</td>
<td>950</td>
<td>-</td>
<td>941</td>
<td>9</td>
<td>-0.95%</td>
</tr>
<tr>
<td>Standard addition</td>
<td></td>
<td>-</td>
<td>942</td>
<td>8</td>
<td>-0.85%</td>
</tr>
<tr>
<td>Medium level molybdenite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Regular procedure</td>
<td>452</td>
<td>-</td>
<td>454</td>
<td>2</td>
<td>+0.44%</td>
</tr>
<tr>
<td>Standard addition</td>
<td></td>
<td>-</td>
<td>464</td>
<td>12</td>
<td>+2.65%</td>
</tr>
<tr>
<td>Low level molybdenite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Regular procedure</td>
<td>292</td>
<td>-</td>
<td>291</td>
<td>1</td>
<td>-0.34%</td>
</tr>
<tr>
<td>Standard addition</td>
<td></td>
<td>-</td>
<td>296</td>
<td>4</td>
<td>1.37%</td>
</tr>
<tr>
<td>MO-1 (MoS₂)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Regular procedure</td>
<td>174</td>
<td>-</td>
<td>167</td>
<td>7</td>
<td>-4.01%</td>
</tr>
<tr>
<td>Standard addition</td>
<td></td>
<td>-</td>
<td>178</td>
<td>4</td>
<td>2.30%</td>
</tr>
<tr>
<td>MO-2 (MoO₂)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Regular procedure</td>
<td>86</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-3.49%</td>
</tr>
<tr>
<td>Standard addition</td>
<td></td>
<td>-</td>
<td>83</td>
<td>3</td>
<td>-3.49%</td>
</tr>
<tr>
<td>MO-3 (MoO₂)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Regular procedure</td>
<td>159</td>
<td>-</td>
<td>154</td>
<td>5</td>
<td>-3.15%</td>
</tr>
<tr>
<td>Standard addition</td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Synthetic ore</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Regular procedure</td>
<td>480</td>
<td>-</td>
<td>480</td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>Standard addition</td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D.C. arc</td>
<td></td>
<td></td>
<td>480</td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>After extraction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>of Re by colorimetric extract-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ing procedure</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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 KReO₄), adding to each 6 ml. of 20 per cent KCNS solution and 2 ml. of 25 per cent of SnCl₂ (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 extraction 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 treatment 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 compared satisfactorily with those of the thiocyanate chemical procedure. The average difference between these two methods was 1.77 per cent.
ACKNOWLEDGMENT

The writer wishes to thank Dr. William G. Schrenk for his aid in the selection of this problem, his liberal donation of time and his helpful suggestions and supervision during this investigation. She wishes also to express her gratitude to Mr. F. N. Ward and Dr. A. T. Myers, U. S. Geological Survey, Denver, Colorado, for furnishing molybdenite samples.
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PLASMA ARC EXCITATION FOR THE SPECTROGRAPHIC DETERMINATION OF RHENIUM

by

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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 HNO₃ 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. Cobalt 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 respectively. 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 determined 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 indicated 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.