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Colorimetric determination of rhenium in ores

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COLORIMETRIC DETERMINATION OF RHENIUM

IN ORES

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Master of Science

by

Clair Winston Rogers

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INTRODUCTION

Since the discovery of rhenium in 1925, by Walter Noddack and Ida Tacke,[1] it has become a very important element of commerce. Compounds of this element have been discovered to be very useful in oxidation reduction reactions. Especially in recent years, sulphides and oxides of this element are being used as reduction catalysts for reducing compounds to their primary hydrocarbons.

Because of the great importance of rhenium there is a necessity for the development of new and better methods for its quantitative analysis. A major problem is the determination of rhenium in the presence of molybdenum, copper and other elements that make it difficult to analyze the content of rhenium in ores. Methods have been developed for this determination in the presence of interfering elements; however, these methods are time consuming, the processes of analysis usually requiring five to six hours.

For these reasons a new and shorter method for the colorimetric determination of rhenium was the object of the research reported in this thesis.

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[1]Hurd, _Journal of Chem. Educ._, _10_, 605-8 (1933).

CHAPTER I

HISTORICAL ASPECTS

A variety of separations and determinations have been developed in the past on a micro as well as a macro scale. Among these, one of the earliest was a distillation method by Geilmann and Weibke, which utilized the technique of passing a stream of moist hydrogen chloride, diluted with carbon dioxide, through a hot concentrated acid solution of perrhenate, followed by a gravimetric determination of the rhenium which collected in the distillate. In another method proposed and advanced by Geilmann and Weibke, molybdenum was separated by precipitation from a nearly neutral solution with 8-hydroxy-quinoline. These methods both worked satisfactorily in the ranges for which they were intended, but when applied to the problem of the separation of larger quantities of molybdic anhydrides from one-tenth of a milligram or less of rhenium, they were not at all satisfactory because molybdenum interferes greatly with the determination.

The developments of Kronman and his students as well as those of Mikhailova, Pevsner, and Archipova, were not satisfactory for low quantities of rhenium and high quantities of molybdenum, because they used a combination of the distillation method with the 8-hydroxyquinoline method to effect the

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determination. Generally the rhenium was determined by a
nitron acetate precipitation. In all these variations on
fundamental methods, none of these workers or their associates
obtained the high-degree of accuracy of separation needed to
make a simple and effective method of determination of rhenium
in the molybdenite minerals. Using these methods the best
that Mikailova, Pevsner and Archipova were able to do was to
determine milligram amounts of rhenium with an accuracy of
0.523%, in the presence of not more than twice as much molyb-
denum as rhenium.[2]

In an early paper by Hurd, it was reported that if a
solution containing molybdenum and rhenium was first treated
with ethyl xanthate, and the molybdenum complex then removed
by extraction with chloroform, rhenium could be determined
with fair accuracy in the remaining solution. The rhenium was
then determined colorimetrically by reaction with stannous
chloride and potassium thiocyanate to develop a colored com-
plex. Neither stannous chloride, hydrochloric acid, ammonium
thiocyanate nor mixtures of the three produced the yellow color
of the rhenium solution with residual traces of xanthate. The
method of Hurd is accurate enough for a qualitative determina-
tion but not for a quantitative analysis. This procedure had
to be refined for use in accurate quantitative work.[3]

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[2]Hiskey and Meloche, Ind. Eng. Chem., Anal. Ed., 12,
503-6 (1940).

[3]Hurd, Ind. Eng. Chem., Anal. Ed., 8, 11-15 (1936).

During the year of 1939, Willard and Smith developed a method whereby the perrhenate could be precipitated from the solution with tetraphenyl arsonium chloride, producing a white crystalline precipitate which is insoluble in cold distilled water. Then the determination is continued by the addition of an excess of tetraphenyl arsonium chloride to the perrhenate, with the volume kept as small as possible. This precipitation of the perrhenate solution is allowed to stand overnight before the rhenium is determined in a hot solution in which the perrhenate complex dissolves. In the work of Willard and Smith, molybdenum apparently did not interfere greatly, but unfortunately it is not possible to precipitate the minute quantities of rhenium usually found in molybdenates. An additional drawback in this method is that of the presence of interfering ions and elements. The interfering ions are permanganate, perchlorate, periodate, iodide, bromide, flouride, thiocyanate, and elements such as mercury, tin, and bismuth also interfere. The nitrate radical must also be absent, except in very low concentration. Interference by molybdenate may also be avoided or counteracted by the use of ammonium hydroxide or tartaric acid as a precipitant.[4]

By using differential reduction with mercury, Hoffman and Lundell were able to make an effective separation of rhenium from its associated elements. Under certain conditions only molybdenate is reduced, and this may be extracted with

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[4]Willard and Smith, Ind. Eng. Chem., Anal. Ed., 11, 305-6 (1939).

ether after the treatment by any thiocyanate. As much as 10 milligrams of molybdenum have been quantitatively separated from 0.001 milligram of rhenium. This method would be satisfactory if the procedure were not so difficult and lengthy.

In 1938, Hurd and Hiskey announced a method capable of determining as little as one part of rhenium in twenty million parts of pyrolusite. In this method rhenium was isolated by an extraction of the thiocyanate complex, followed by a modified distillation procedure. If very little or no molybdenum was present in these minerals, the difficulty of separation was not extremely great; therefore the method, although somewhat bulky and cumbersome to use, was satisfactory.[5]

Near the end of 1949, Hickey and Meloche reported a process or method of determining five microgram amounts of rhenium in the presence of million-fold excesses of molybdenum. Their method combines a modified distillation and a modified colorimetric technique; it has been applied to the analysis of twenty-eight molybdenate complexes. In the first place, there is enough chemical similarity between rhenium and molybdenum to make a clear cut separation somewhat difficult. In the second place, although the molybdenate contains the highest natural concentrations of rhenium that have been found, the rhenium must still be separated from the molybdenate minerals. These concentrations of rhenium are of the order of 0.0001% to 0.001% of the total ore content. In addition, no colorimetric reaction for the determination of rhenium had been

[5]Hiskey and Meloche, op. cit., pp. 503-6.

developed, up to this point, wherein molybdenum did not inter-
fere. Consequently, it became necessary to eliminate molyb-
denum before any rhenium estimation could be made, and it is
in this operation that most of the difficulty arises. The
combined distillation colorimetric method was developed to
eliminate any interference by molybdenum.[6]

Melaven and Whetsel, in 1948, proposed and described
a method for the quantitative colorimetric determination of
rhenium in solutions containing up to 0.9 milligram of rhenium
in the presence of not more than one milligram of molybdenum
in a total volume of 100 ml. In this determination or process
the molybdenum was precipitated from a four to seven normal
sulphuric acid solution by alpha-benzoinoxime, and separated
from the rhenium by filtration. The determination of rhenium
was by the formation of the rhenium thiocyanate color complex
and the measurement of transmittance of the solution by means
of a photoelectric spectrophotometer. A precision of plus or
minus 2% has been obtained over specified concentration ranges.
This method is not recommended for samples containing more
than one milligram of molybdenum.

In order for molybdenum to precipitate with alpha-
benzoinoxime, the original volume of 25 ml. of solution should
be at least four normal with respect to sulphuric acid; other-
wise the intensity of the color is proportional to the acid
concentration. In the concentration range of four to seven
normal the intensity of the color is fairly constant at

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[6]Ibid.

specific rhenium concentrations. It is desirable that no excess reagent crystallize out of solution during the development of the color. One and a half hours are sufficient for the filtrate to stand, but no harm is done if it stands longer. The volume of the filtrate is 100 ml., including the wash solution to prevent any appreciable recrystalization of the reagents upon the dilution that follows the development of the color. Control of the time between the development of the color and the second filtration is not necessary as long as ten to fifteen minutes elapse between the two operations. Although the intensity of the color is almost constant one hour after its development, there is a gradual change in the presence of light. Therefore, the time between the development of the color and the measurement of the transmittance should be kept reasonably constant for all sample solutions. During this time the colored solution should not be allowed to stand in direct sunlight, because its color slowly fades upon exposure to light.[7]

The latest and apparently the most useful method is now being used by Kennecott Copper Corporation. It was developed for use with high molybdenum content ores by E. E. Malouf and M. B. White. This method developed and described for the quantitative colorimetric determination of rhenium is used for samples containing as little as 0.1 milligram to 2.5 mg. of rhenium. Determinations of rhenium have been made in the

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[7]Melaven and Whetsel, Anal. Chem., 12, 1209 (1948).

presence of 1.25 mg. of molybdenum in a total volume of 25 ml. of solution. The molybdenum is separated from the rhenium as a metalorganic compound formed with ethyl xanthate and extracted from a dilute acid solution with an organic solvent solution such as a one-to-one solution of carbon tetrachloride and benzene mixture. The rhenium is determined by the formation of a rhenium thiocyanate color complex and the measurement of the transmittance of the solution by means of an electrophotometer. The precision of this method is plus or minus 2% over a specified concentration range. This method is readily applicable to the mass analysis technique of routine analytical laboratories. The chief drawback of this method is that it takes a minimum of four to five hours to complete the analysis after the preparation has been made.[8]

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[8]Malouf and White, Anal. Chem., 23, 497-9.

CHAPTER II

METHOD AND MATERIALS

Method

In searching through the chemical literature, it was found that the methods previously discussed for the most part were unsatisfactory. Molybdenum in these determinations was the element that interfered most in making the colored complex with rhenium. The research for the contents of this thesis dealt with the problem of determining rhenium in ores containing molybdenum, copper, etc., by the use of dimethylglyoxime as a complexing compound with rhenium. It was found that copper complexed with dimethylglyoxime to a far greater extent than did molybdenum. The molybdenum percentage must be very high to interfere greatly with the rhenium determination. Although copper interfered greatly, it could be eliminated by a strong alkaline fusion of the sample with sodium hydroxide and sodium peroxide. Because these compounds, used for fusion, are extremely basic, the $_pH$ of the fusion solution is very high. Copper precipitates as a hydroxide from this strongly basic solution upon the addition of excess sodium peroxide. Other ions are also carried down by this copper hydroxide precipitation. The ions which otherwise would cause this determination to be inaccurate are eliminated in one operation.

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Thus, the method discussed within this thesis appears to be the shortest and easiest procedure yet reported.

The rhenium content of synthetic or theoretical ore samples was measured by means of a Colemann Spectrophotometer after fusion and neutralization. Before measuring the optical density of the solution, reduction of the rhenium with stannous chloride and complexing with dimethylgloxime was necessary.

Materials

Preparation of Required Reagents

Stannous Chloride Solution: A 35% solution of stannous chloride was prepared by weighing 82.2 grams of stannous chloride dihydrate into a 200 ml. volumetric flask. Fifty ml. of concentrated hydrochloric acid was added to dissolve the stannous chloride. Then distilled water was added and the solution was mixed thoroughly and diluted to the mark on the flask with one-to-one hydrochloric acid solution. This reagent was used to reduce the valence of rhenium. A few pieces of mossy tin were added to prevent oxidation of this stannous chloride solution.

Dimethylglyoxime Solution: 11.6 grams of C.P. dimethyl-glyoxime powder were weighed into a liter volumetric flask, 500 ml. of 95% ethyl alcohol was added and the mixture was heated to dissolve the dimethylglyoxime. The solution was di-luted to the mark with additional ethyl alcohol.

Sodium Hydroxide: Either practical or analytical grade sodium hydroxide was used for fusion of the sample of ore.

Sodium Peroxide: Sodium peroxide was used in the final fusion and also for precipitation of any copper not precipitated by sodium hydroxide alone.

Sulphuric Acid: Concentrated sulphuric acid is used for the neutralization of the basic sample following fusion.

Apparatus and Equipment Required

A high temperature burner: 900° to 1500° temperature capacity used for the fusion of an ore material.

An iron crucible: (60 ml. capacity) Used to contain the sample during fusion.

A cast iron plate: Used to cool the molten sample immediately after fusion.

A #2 or #75 mm. Buchner funnel and filter flask: Used for the extraction of hydroxides and oxides from the fusion solution.

Three 50 ml. capacity burets graduated to tenths of ml.: Used for the preparation of analysis samples.

Spectrophotometer (Colemann Universal): P.C. - 4 filters are used in this determination.

Plus ordinary laboratory apparatus: Pestle and mortar; chain-matic beam balance; platform scale; box of fine 75 mm. Buchner paper; 100 ml. graduated cylinder (pyrex); hot plate; 5 liter capacity rock crock; 500 ml. capacity polyethylene wash bottle; two Lincoln clamps; a wire gause; glass stirring rod with rubber policeman; spatulas; and sample spoons.

CHAPTER III

EXPERIMENTAL RESULTS AND CONCLUSIONS

Standard Curves

In order to establish the correct wave length at which this determination should be performed it was necessary to establish the point of minimum transmittance for the dimethylglyoxime complex of rhenium. This was done by running a series of spectral curves of standard solutions of known concentrations. The procedure for running these standard spectral curves was as follows: A standard solution containing one hundred parts per million (ppm) of rhenium was made by weighing 0.1553 g. of potassium perrhenate into a liter volumetric flask and diluting to the mark with distilled water. A ten ppm solution was made by measuring 50 ml. of the 100 ppm solution with a buret, into a 500 ml. volumetric flask and diluting to the mark with distilled water. Fifty ml. portions of the one, two, three, four, and five ppm standard solutions were prepared by dilution of the 10 ppm standard solution; and 50 ml. portions of ten, twenty, thirty, forty, and fifty ppm standard solutions were prepared by dilution of the 100 ppm standard. Prior to dilution to the mark one and one-half ml. of 35% stannous chloride and one and one-half ml. of 0.2 normal dimethylglyoxime alcohol solution was added to each of

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these 50 ml. flasks in that order. Each flask was then heated
on a hot plate, just to boiling, to develop the full color,
then cooled rapidly and filled to the mark with distilled
water. The optical density of each solution was then deter-
mined with the Colemann Universal Spectrophotometer using a
blank consisting of all the components of the solution except
rhenium. The optical density of each of the solutions was
measured over a spectral range of 400 to 550 mu. and plotted
against the wave length. The minimum transmittance for all
of these solutions was found to be at a wave length of 455 mu.
(see Figures 1 and 2). By plotting optical density against
concentrations at 455 mu. as shown in Figures 5 and 6, a curve,
which is termed a working or determinative curve, was obtained.
This curve was used for the analysis of solutions of unknown
concentrations. The optical density of an unknown solution
was determined and its concentration of rhenium read from the
graph.

Fusion and Preparation of Ore Sample

The procedure and method that follows is that used for
rhenium samples containing interfering elements, mainly: iron,
copper, molybdenum nitrates, sulphur, and other trace and rare
earth elements. A typical ore sample might weigh 1.25 g.
Such a sample was prepared by mixing 0.5720 g. of equal por-
tions of copper sulfate and copper nitrate, 0.6304 g. of an
equal mixture of iron sulfide and raw material such as might
come from a mine, 0.01 g. of molybdenum oxide which is present

in most ores containing rhenium, and 0.0388 g. of potassium perrhenate in an iron crucible. To prepare for the fusion, 5.0 g. of practical or analytical grade sodium hydroxide was added to the crucible containing the sample or ore. The sample was fused, using a high temperature burner of 900° centigrade capacity. The sample was heated slowly at first and then, after the material had been dissolved by the sodium hydroxide, the temperature of the mixture was raised to allow the removal of gaseous oxides and sulfides which, if not eliminated, might have interfered with the complexing action in the final solution. After the material had ceased to effervesce and became homogeneous, five grams of C.P. sodium peroxide was added with extreme caution and the mixture heated at high temperature to remove any additional gases that might still be in the mixture. When the crucible was red hot and effervescence had ceased, the contents of the crucible were poured out on a clean cast iron plate. Exercising care not to lose any material that might be on its outside, the crucible was placed in a 400 ml. beaker and the beaker covered with a watch glass. After the fused material and the crucible in the beaker had cooled completely, the crucible was removed from the beaker, filled half full of distilled water, and heated to boiling to remove the rest of the fused material from the crucible. The hardened fusion cake was removed from the iron slab, placed in an 800 ml. beaker, and the boiling water from the crucible poured into the beaker containing the cake. The beaker was quickly covered with a watch glass to prevent spattering of the material from

the beaker. Distilled water, sufficient to fill the crucible half full, was added, boiled and poured into the beaker. To make sure all the material had been removed from the crucible this procedure was repeated several times, scraping down the sides of the crucible with a stirring rod and rubber policeman each time.

The precipitate which forms upon the addition of water contains hydroxides of copper, iron, molybdenum, and other rare earth elements. However, the pH of this solution is not right for the precipitation of all the copper, which interferes the most in this determination. The addition of 0.4 g. more of sodium peroxide to the solution of the fusion material was found to make the pH just right to precipitate the rest of the copper from the solution. The precipitate is a deep reddish brown and is predominantly iron hydroxide. After the precipitation of the hydroxides the solution was boiled with chopped up filter paper, or filter-aides, for twenty minutes. The solution was then filtered through a 75 mm. Buchner suction funnel using high suction to facilitate ease of filtration. The precipitate was then washed with three different portions of boiling water to remove all the soluble materials including rhenium. This boiling is required to precipitate all the copper and molybdenum. If it is boiled less than twenty minutes the color of the copper ion remains in the solution. The filtrate is placed in an ice bath overnight. A precipitate of iron hydroxide should form, and should be removed by filtration with a Buchner funnel with suction and washed with distilled

water. The solution is extremely basic, having a $_pH$ of 12.5, and is neutralized with concentrated sulphuric acid (the use of hydrochloric acid must be avoided in this neutralization). Hydrochloric acid was used to neutralize one fusion solution, but it caused the intensity of coloration to be too great, giving a greater optical density than for the same concentration of the standard solution of rhenium. Sulphuric acid does not interfere with the formation of the dimethylglyoxime complex of rhenium. After the neutralization, the solution is placed in a 250 ml. volumetric flask and diluted to the mark with distilled water. This solution theoretically contains 100 ppm of rhenium.

To prepare solutions for the determination of rhenium, using dimethylglyoxime as the complex compound, a ten ppm solution of rhenium in addition to the 100 ppm of rhenium fusion solution is made by measuring 50 ml. of the 100 ppm solution of rhenium into a 500 ml. volumetric flask and diluting to the mark with distilled water at room temperature. One, two, three, four, five, ten, twenty, thirty, forty, and fifty ppm samples are prepared in 50 ml. volumetric flasks by diluting aliquots of the ten ppm solution and 100 ppm solution following the procedure used to make the solutions for the standard curves. Distilled water was added to make a total volume of 25 ml. in each flask.

As in the preparation of the standard solutions 1½ ml. of stannous chloride and 1½ ml. of dimethylglyoxime were added to each of these ten flasks in that order. Each solution was

heated just to boiling to bring out the full color and then cooled rapidly. The stannous chloride is 35% in a one-to-one hydrochloric acid solution, and the dimethylglyoxime is 0.2 normal in an ethyl alcohol solution. Rapid cooling is necessary in order to minimize the evaporation of the alcohol.

The solutions were ready for analysis following dilution to the marks on the volumetric flasks. The colorimetric analysis must be made three to four minutes after the final addition of distilled water. The reason for not adding the distilled water until the analysis is to be made is that a finely divided precipitate forms in the flask approximately four minutes after dilution. If the analysis is not made within the designated time period after the final dilution, the results will not correspond to those obtained with the standard solutions. This determination is satisfactory for concentrations of rhenium in the solution up to about 25 ppm. Above this concentration a precipitate forms too rapidly following the addition of the final 25 ml. of water to make accurate analysis possible (shown by the branching of the curve in Fig. 5). In order to find out whether or not the point of minimum transmittance of the fusion solutions corresponded with that of the standard solutions (a wave length of 455 mu. as shown by the standard spectral curves in Figs. 1 and 2), spectral curves were run using the fusion solutions described above over a range of 400 to 550 mu. A plot of optical density versus wave length for each of seven fusion solutions (Fig. 1) (the last three precipitating too fast to obtain a

curve) showed that the minimum transmittance for these solutions was also at a wave length of 455 mu. (see Figs. 1 and 3). Because the points of minimum transmittance or maximum optical density of the standard and fusion solution are the same for the rhenium samples up to twenty ppm, it was possible to obtain a working or determination curve for the fusion solution which corresponded exactly to that of the standard working curve, as shown in Figs. 5 and 6.

Discussion

In the fusion process it was found that ore samples of 1.25 g. fused with 5 g. of sodium hydroxide gave the best results. The reason for this is that too large an ore sample produces precipitates and filtrates which are too bulky to handle efficiently. Too small a sample causes small amounts of sodium hydroxide to spatter out of the crucible, thereby causing a loss of rhenium from the sample and producing an inaccurate analysis. It was found that the sodium peroxide used for the elimination of copper hydroxides must be added after fusion is completed, that is, to the fusion solution. The minimum amount necessary was found to be 0.4 gram; any less than this had little effect upon the precipitation of copper salts as the hydroxide. After the peroxide is added, the solution must be boiled for at least twenty minutes to coagulate and precipitate all the oxides and hydroxides of the different elements and to rid the solution of the blue copper color. If copper ion color remains in the solution the copper will complex with the dimethylglyoxime along with rhenium and

cause a spectral shift to a shorter wave length at maximum
optical density or minimum transmittance, as shown in Fig. 4.
The copper complex with dimethylglyoxime shows the highest
optical density at a wave length of 380 mu. (Fig. 4, part 1),
while the minimum transmittance for the rhenium complex is at
a wave length of 455 mu., as shown by Fig. 4, part 2. When
copper and rhenium are added together, the optical density is
almost twice as great as when they are run separately, and
there are two peaks in the composite curve at wave lengths of
390 mu. and 440 mu., as shown in Fig. 4, part 3. Thus, one
can see by the overlapping of these curves (Fig. 4) that copper
interferes greatly in this determination.

The main purpose for the cast iron plate is to provide
for rapid cooling of the fused material, as it does not adhere
to a cold cast iron plate. If the material were cooled in the
crucible, it would be very difficult to remove it.

If the solutions are warm, very small amounts of iron
hydroxide will remain dissolved. In order to remove this dis-
solved hydroxide, an ice bath should be used to precipitate
the remaining iron hydroxide. The solution is allowed to stand
for at least eight to twelve hours, or overnight in the ice
bath.

Sulphuric acid must be used for the neutralization of
the basic fusion solution in order to obtain the same intensity
of coloration with dimethylglyoxime as that obtained with the
standard solution. If hydrochloric acid is used for this
neutralization process, the intensity of the color with some

of the concentrations is too great, while with other concentra-
tions the coloration is too small.

The dimethylglyoxime solution is prepared with 95%
ethyl alcohol in order to sustain the coloration without fad-
ing. The alcohol, however, causes the precipitation which
follows the addition of the final amount of water to each of
the samples in the determination. A test was made to deter-
mine whether or not acid could be used as a solvent for the
dimethylglyoxime instead of alcohol and thereby prevent this
rapid precipitation. When sulphuric acid was used to dissolve
the dimethylglyoxime the coloration in the samples was too
intense; however, no precipitation was produced after the solu-
tion stood for a long period of time. When hydrochloric acid
was used, the intensity of coloration was light and continued
to fade, but a precipitate was not formed. The conclusion was
drawn that alcohol must be used even though it causes a preci-
pitate to form after a few minutes.

Conclusions

The method now being used in industry takes four to
five hours to determine the rhenium content in the ores after
the sample has been dissolved, because of the time needed to
eliminate interfering elements. After all these elements are
out of the solution, the method has an accuracy of plus or
minus 2 per cent, and the coloration with potassium thiocyanate
takes place in the presence of 100 to 1000 parts per million
of rhenium.

In this determination after the fusion cake has been

dissolved and the solution prepared, the determination of rhenium content takes a maximum of ten to fifteen minutes. The accuracy of this method is at least plus or minus 1 or 2 per cent for concentrations of rhenium from one to twenty-five parts per million. One part per million or less of rhenium may be detected and measured by this method. It is very accurate for concentrations of rhenium from one to twenty-five parts per million.

Irritating compounds, used for the elimination of interfering elements in previous methods of determination, can be omitted by the use of the method herein described. This method should save time, money, and labor.
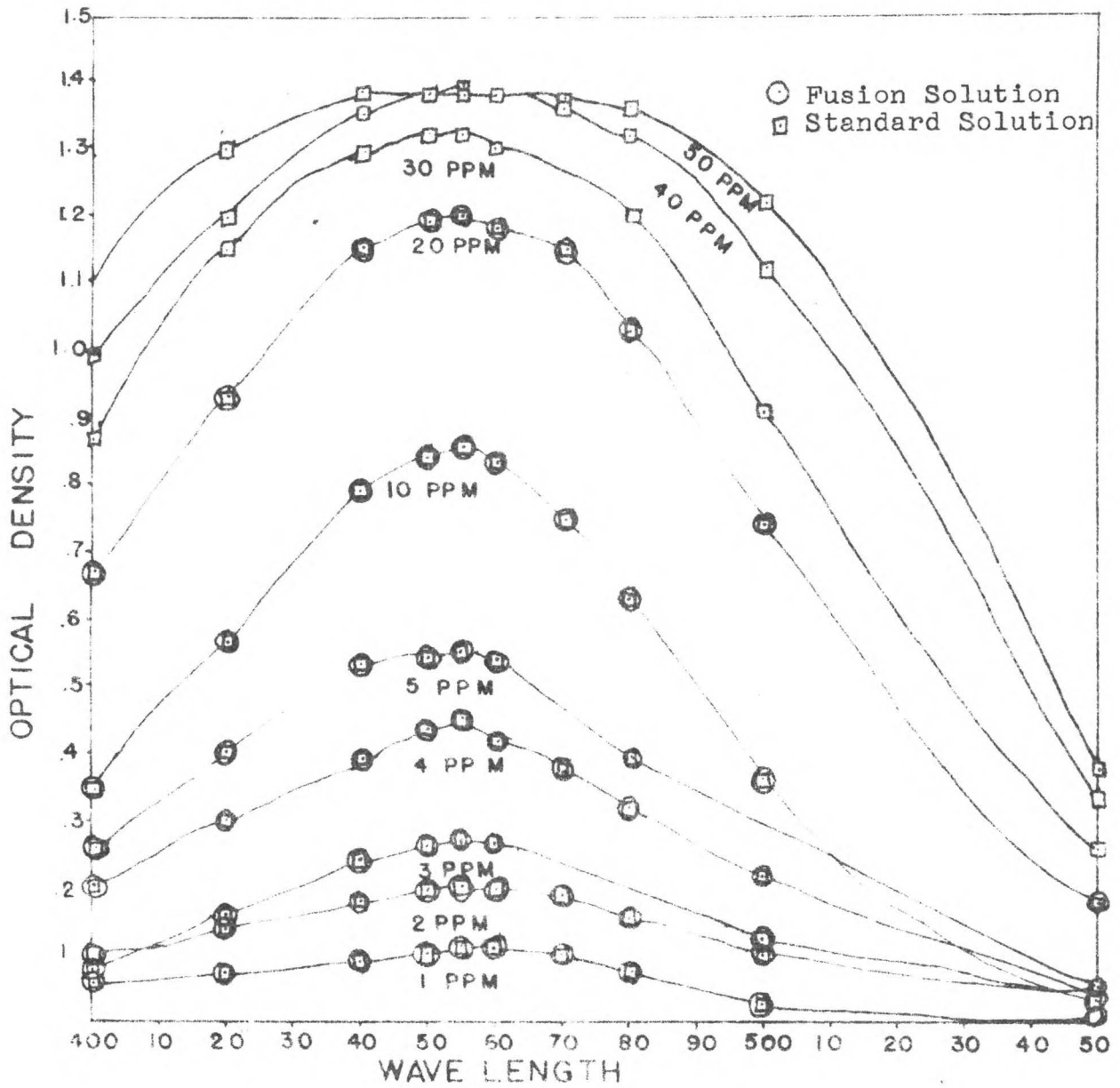
Fig. 1.--Spectral curves for both standard and fusion solutions. Optical density versus wave length for specific concentrations of rhenium.
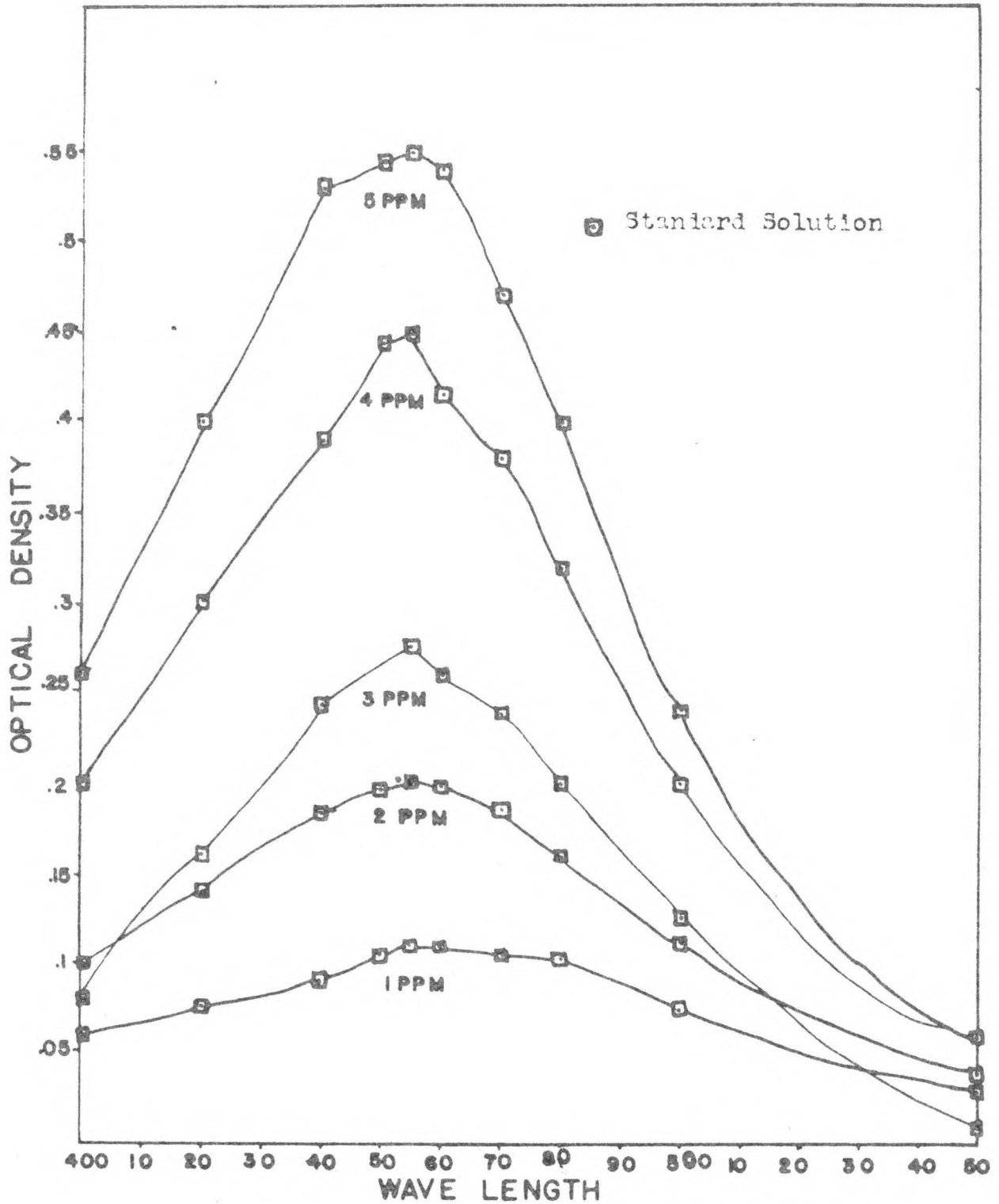
Fig. 2.--Spectral curves of the standard solution.
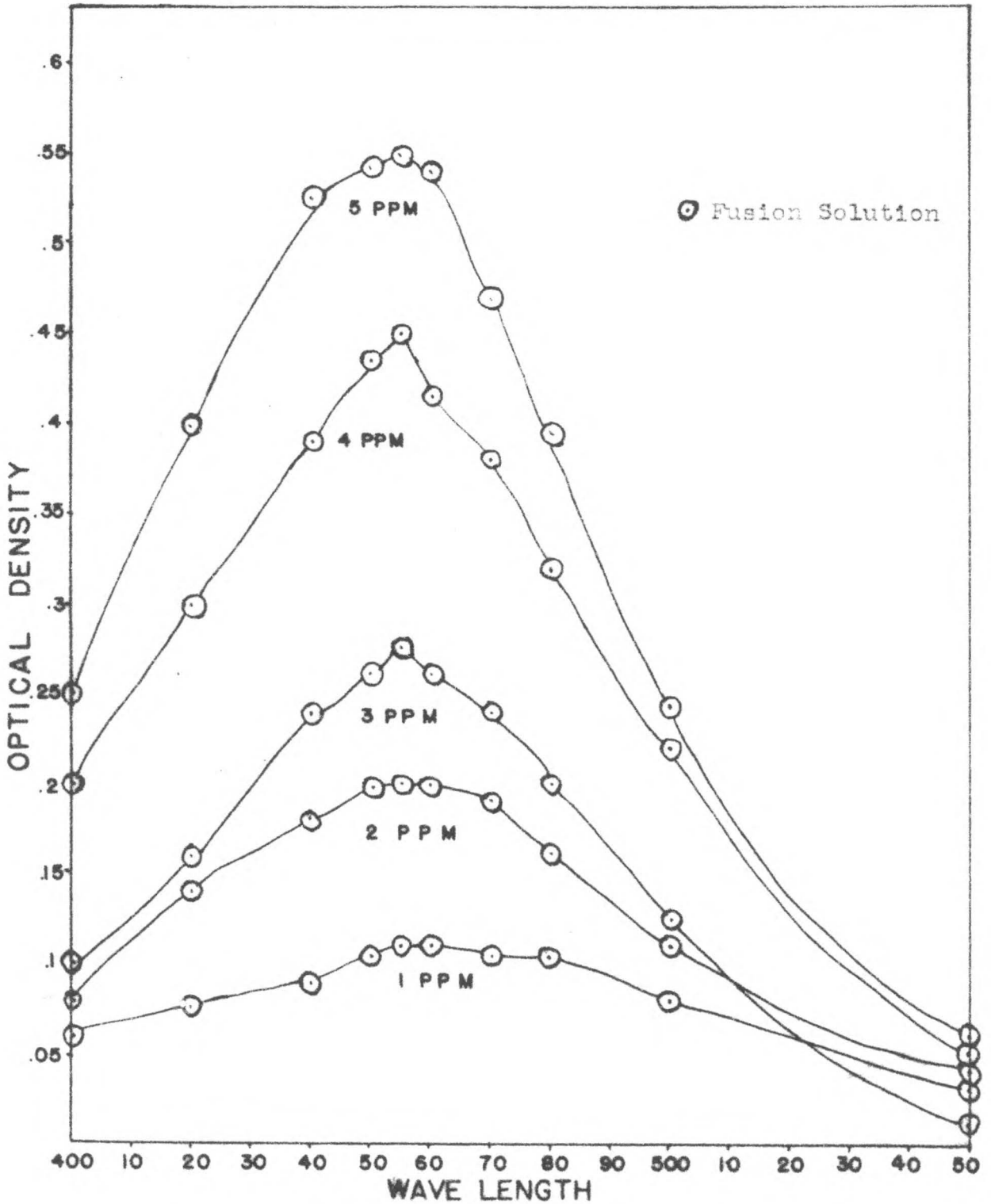Plot of optical density versus wave length for specific
concentrations.

Fig. 3.--Spectral curves for the solution of ore-like material after fusion. Plot of optical density versus wave length for specific rhenium concentrations.
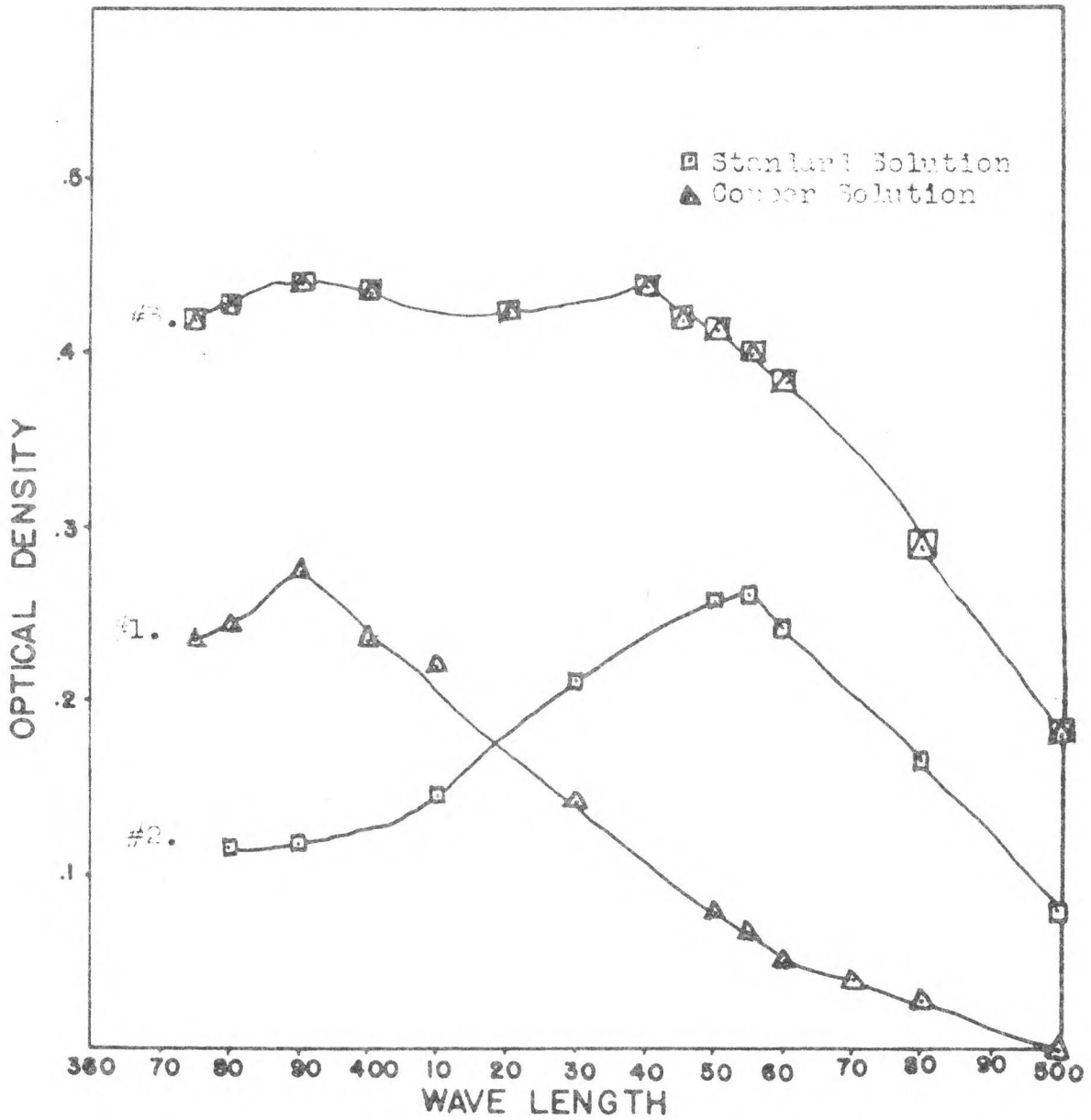
Fig. 4.--Plot of optical density versus wave length,
illustrating the interference of copper.
1.   .005 gr. of cu./50 ml. of solution.
2.   2.5 ppm of rhenium in solution.
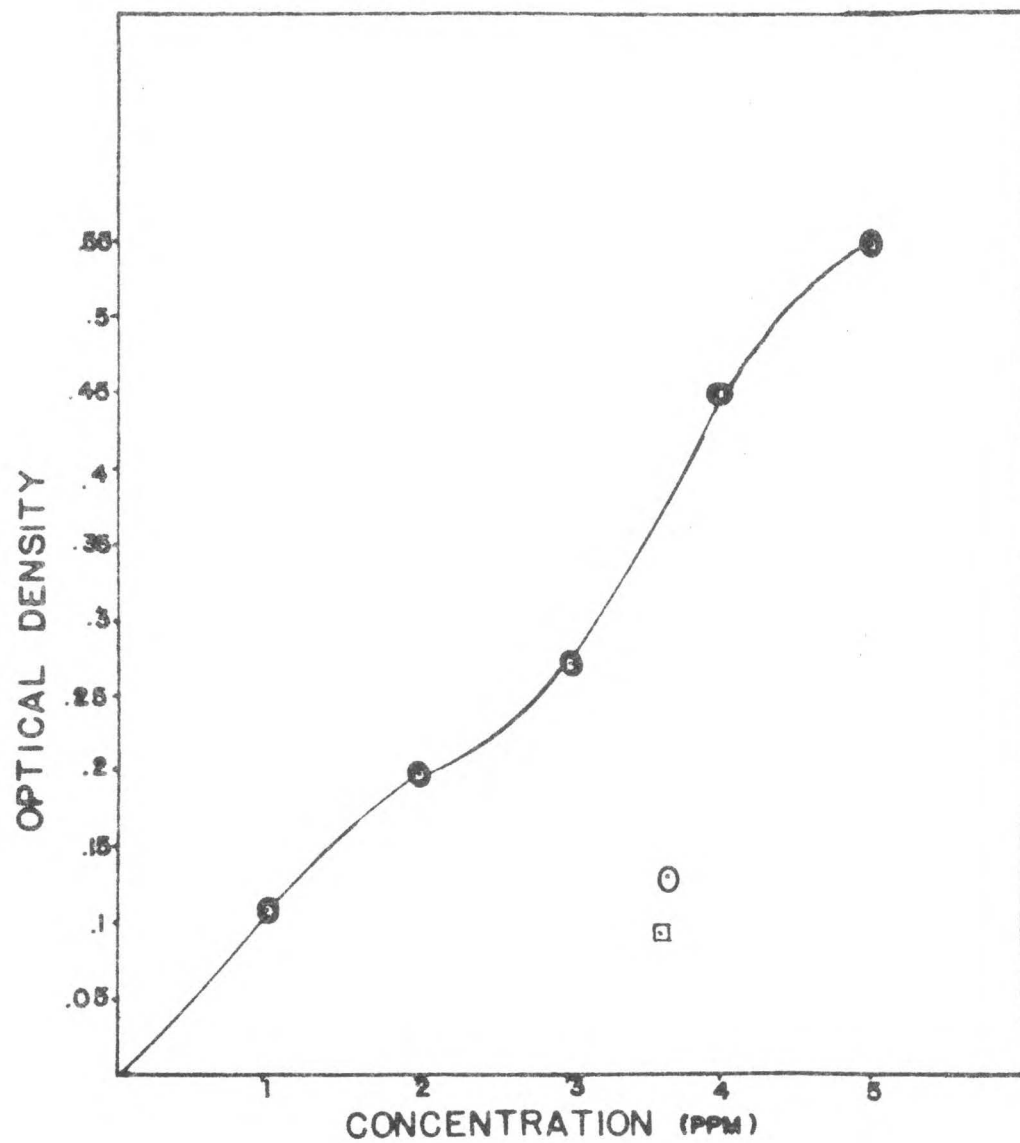3.   Curve of one and two mixed together.

Fig. 6.--Optical density versus rhenium concentration.

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COLORIMETRIC DETERMINATION OF RHENIUM

IN ORES

An Abstract

of a Thesis Submitted to

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Master of Science

by

Clair Winston Rogers

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ABSTRACT

The problem of colorimetrically determining rhenium in the presence of molybdenum, copper, iron, sulphur, and rare earth elements with the use of dimethylglyoxime as the complexing compound was accomplished by the method reported herein. The interfering elements were eliminated either as gaseous oxides and sulfides or were precipitated from a highly basic solution by means of a strong alkaline fusion of equal weights of sodium hydroxide and sodium peroxide, and the ore sample containing rhenium. The fusion product was dissolved in water, the solution boiled with a slight excess of sodium peroxide, and the hydroxide of all the interfering ions precipitated. The filtrate was neutralized with sulphuric acid after the precipitate had been removed and thoroughly washed. Aliquot portions of this solution were then diluted to specified concentrations in fifty ml. flasks. Stannous chloride was used for the reduction of rhenium to an oxidation state wherein it forms a colored complex with dimethylglyoxime. The optical density of the rhenium color complex was measured with a Coleman Spectrophotometer and compared with the optical density of the same concentration of standard solution. The optical densities of the fusion rhenium solutions were exactly equal to those of the standard solutions of equal rhenium

concentration up to about twenty-five parts per million. This method appears to give very accurate results for the determination of rhenium up to this concentration.