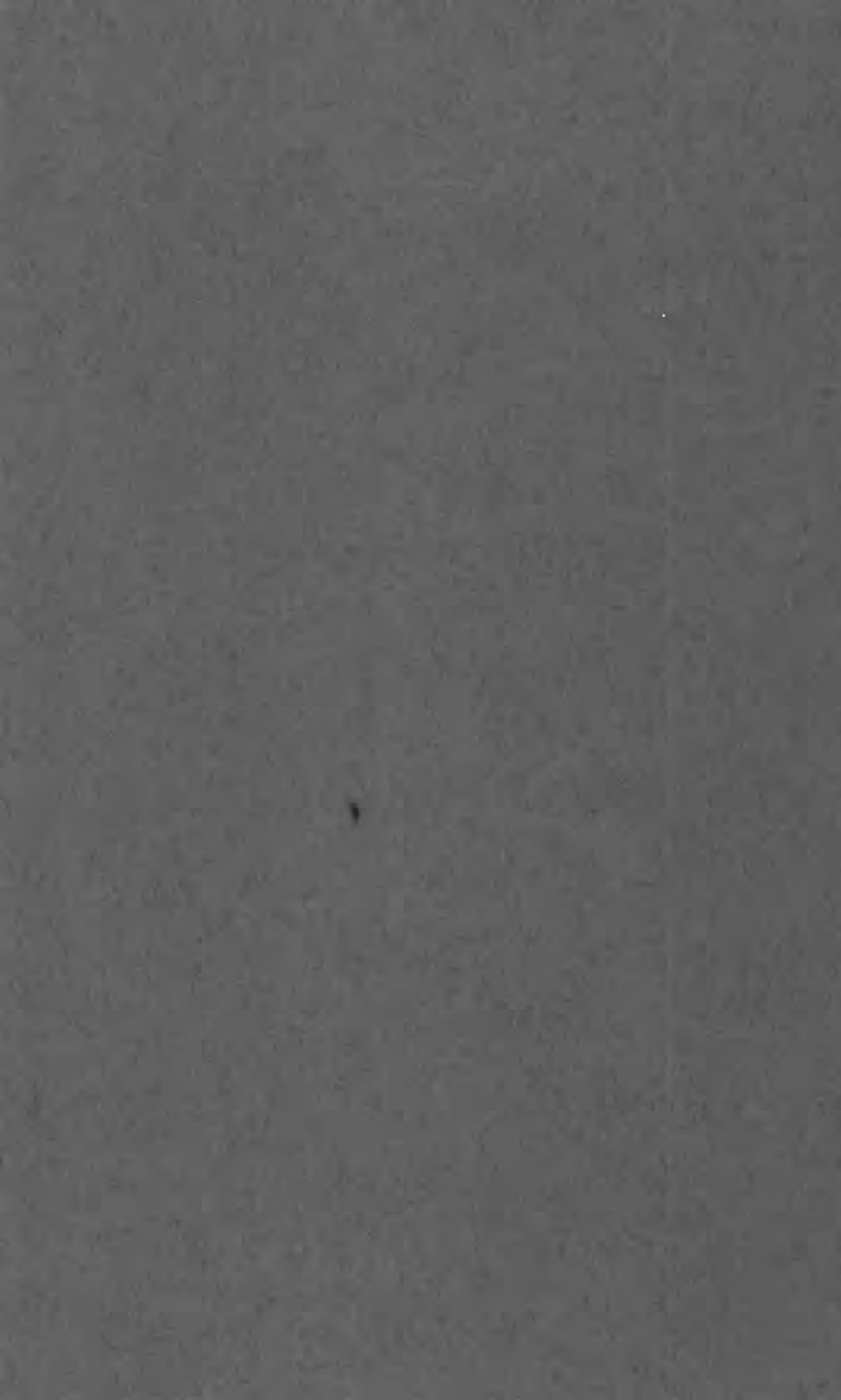


Rapid Analysis of Chromite and Chrome Ore

GEOLOGICAL SURVEY BULLETIN 1084-B





ERRATA

Rapid Analysis of Chromite and Chrome Ore, by
Joseph I. Dinnin. U. S. Geological Survey Bulletin

1084-B

Page 45:

Under "Procedure (Cr_2O_3 in separate sample)",
item 3 should read:

3. Mix thoroughly with a platinum rod and cover
with a suitable lid.

Under "Calculation of percent Cr_2O_3 " the equation
should read:

$$\text{Percent } \text{Cr}_2\text{O}_3 = \frac{\text{ml dichromate} \times 2.534 \times 100}{\text{sample wt (mg)}}$$

Rapid Analysis of Chromite and Chrome Ore

By JOSEPH I. DINNIN

CONTRIBUTIONS TO GEOCHEMISTRY

GEOLOGICAL SURVEY BULLETIN 1084--B

A discussion of rapid methods of laboratory analysis for determining the major and some minor constituents of chromite and chrome ore



UNITED STATES DEPARTMENT OF THE INTERIOR

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GEOLOGICAL SURVEY

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The U.S. Geological Survey Library has cataloged this publication as follows:

Dinnin, Joseph Isadore, 1920-

Rapid analysis of chromite and chrome ore. Washington,
U. S. Govt. Print. Off., 1959.

iv, 31-68 p. diagrs., tables. 25 cm. (U. S. Geological Survey.
Bulletin 1084-B. Contributions to geochemistry)

Bibliography: p. 66-68.

1. Chromite. 2. Chromium. 1. Title. (Series: U. S. Geological Survey. Bulletin 1084-B. Series: U. S. Geological Survey. Contributions to geochemistry)

549.52

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CONTRIBUTIONS TO GEOCHEMISTRY

RAPID ANALYSIS OF CHROMITE AND CHROME ORE

By JOSEPH I. DINNIN

ABSTRACT

Rapid methods for the determination of the major and of some minor constituents of chromite and chrome ore permit the complete analysis of a dozen or more samples to be performed in about 5 days with a precision comparable to that of the more conventional methods. The sample is fused with sodium peroxide in a zirconium crucible. The major constituents are determined from aliquots of a single solution of sample prepared by acidifying a water extraction of the fusion product. Cr_2O_3 is determined volumetrically by ferrous ammonium sulfate—dichromate titration; SiO_2 is determined spectrophotometrically using the reduced silicomolybdate color; total iron is determined by a modified differential spectrophotometric method using orthophenanthroline. An additional aliquot, electrolyzed in a mercury cathode apparatus, is used for the titration of MgO with Versene, and for the spectrophotometric determinations of Al_2O_3 and TiO_2 with alizarin red-S and Tiron, respectively. The minor constituents are determined on another aliquot from which CrO_2Cl_2 has been volatilized by fuming with HClO_4 and HCl ; MnO , V_2O_5 , and NiO are then determined spectrophotometrically using the permanganate, phosphotungstovanadate, and α -furildioxime colors, respectively. Separate portions of sample are used for the determination of CaO by Versene titration, H_2O by the Penfield tube method, and FeO by one or more methods. The precision of the method was tested by comparing the results of the rapid procedures with those obtained by conventional procedures on standard materials.

INTRODUCTION

GENERAL DISCUSSION

The critical need for chrome ore in the United States has greatly increased the U. S. Geological Survey projects for locating new deposits of ore and for the study and delineation of known deposits. To cope with an increased demand for complete chemical analyses of chromite, the Survey instituted a program aimed at increasing the speed and accuracy of chromite analysis.

Various methods and schemes of analysis were critically studied. The most satisfactory were rigorously tested on previously analyzed materials. A description of the current status of the methods is presented here.

In this description the term "chromite," following the recent usage recommended by Thayer (1956, p. 14), refers to the mineral chromite. To distinguish between the mineral and the commercial ore, which is also commonly referred to as chromite, the ore is designated "chrome ore."

Although the methods outlined here are described as being rapid, rapidity of execution was not the main criterion used in the selection of each procedure. Precision and reliability under routine conditions were primary considerations in the selection. A more rapid procedure was selected only if the precision and reliability were at least equal to that of the conventional procedure.

The study of rapid methods for the analysis of chromite is related to a general program of the U. S. Geological Survey which involves the re-examination of existing procedures in the light of recent advances in analytical techniques. A description of a major phase of this re-examination, applied to silicate rocks, was recently published (Shapiro and Brannock, 1956).

The procedures used for the analysis of chromite were designed so that they could be performed by techniques and with reagent solutions similar to or identical with those used for silicate rocks. Most of the procedures are the same as those used in rapid analysis of silicate rocks; a number of the procedures have, however, been modified in order to cope with the different interferences or different concentrations of the elements being determined. Two of the procedures have been adapted from metallurgical or trace element analysis.

The inherent advantages of the rapid silicate methods have been retained. With minor exceptions the determination of all of the constituents are direct and are not dependent upon the completeness of prior separations. Because of the independence of each of the determinations the summation of the results is more likely to give some indication of the quality of the determinations than does a summation based on gravimetric separations.

The nature of the methods is such that the analysis of a dozen samples can be performed with only a relatively small increase in time over that required for the analysis of a few samples.

The number of samples that can be handled at one time depends mainly upon the amount of equipment available. A group of 10 samples can usually be handled conveniently. As many as 30 samples have been handled at one time without causing undue scheduling complications.

After the equipment is set up and most of the stable reagent solutions have been prepared, one analyst can analyze at least a dozen samples for their major constituents in about 5 days.

The procedures described here provide for the determination of Cr_2O_3 , Al_2O_3 , SiO_2 , Fe (total), FeO , MgO , TiO_2 , MnO , V_2O_5 , NiO , CaO , and H_2O . A flow diagram outlining the major steps in the analysis is shown in figure 5.

The major part of the analysis is made on one principal solution, designated "solution A." Aliquots of this solution are used directly for the determination of SiO_2 and total Fe. A third aliquot, after auxiliary oxidation, is used for the determination of Cr_2O_3 . A fourth aliquot is electrolyzed in the mercury cathode apparatus and the residual solution is designated "solution B." Aliquots of solution B are used directly for the determination of Al_2O_3 , MgO and TiO_2 .

Several minor elements usually occur in chromite and chrome ore. In this laboratory these elements, namely, Ca, Mn, V, and Ni, are usually determined spectrographically. Methods for their chemical determination may be of interest to laboratories which do not have spectrographic facilities available. These methods have also been integrated into the general scheme of analysis. An additional aliquot of solution A is evaporated and fumed with perchloric, hydrofluoric, and hydrochloric acids. Aliquots of this solution, designated "solution C," are used for the determination of MnO , V_2O_5 , and NiO .

Ferrous iron, CaO , and total water are each determined on separate samples.

Three methods are presented for the determination of ferrous iron. This has been done because the author feels that no one method for this determination is itself reliable enough to give trustworthy results. One of the criteria of an accurate analysis is that the same result should be obtained no matter what method is used for the determination.

Hartford (1953) and Reelfs (1956) have described many of the current methods for the analysis of chromite used by industrial and other laboratories in this country and abroad. Harpham (1955) has reviewed many of the methods available for decomposing chromite for analytical purposes. As these publications present an excellent review and critique of present and past analytical practices, no such review is presented here. However, mention should be made of an interesting new scheme for the complete analysis of chromite recently described by de Wet and Van Niekerk (1952). They make extensive use of a centrifuge to facilitate many of the time consuming separations. A sodium hydroxide plus sodium peroxide decomposition of one sample is used for the determination of chromium and iron after centrifugation of the alkaline suspension into two parts. A second sample, similarly separated, is used for the determination of alumina and titania; alumina is determined gravimetrically in the liquor by precipitation as aluminum benzoate; titania is determined in the sediment colorimetrically as the peroxide. A third sample, decomposed with

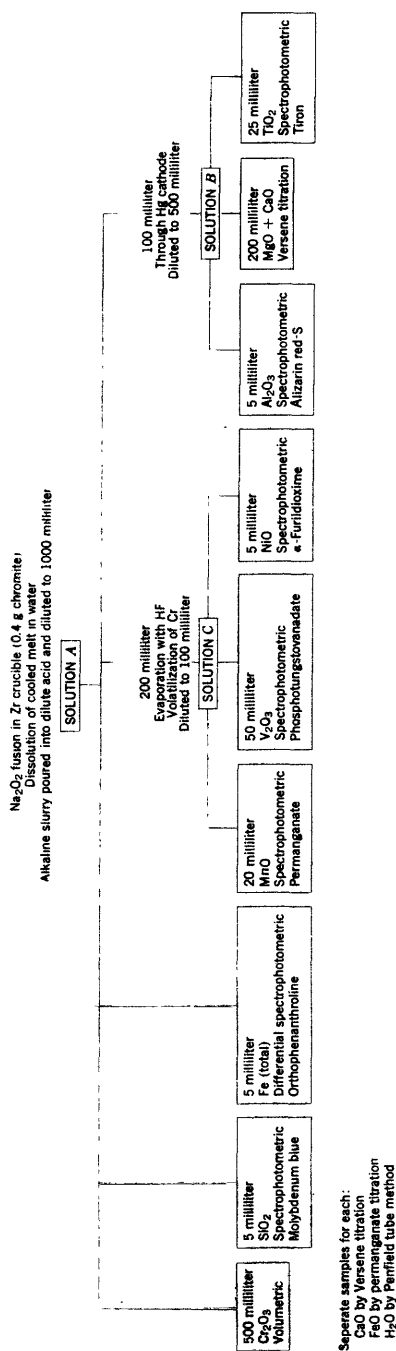


FIGURE 5.—Outline of rapid methods for the analysis of chromite and chrome ore.

potassium bisulfate, is used for the gravimetric determination of magnesia as the phosphate.

PRECISION AND ACCURACY OF CURRENT METHODS OF ANALYSIS

Hartford (1953) has provided some valuable information on the precision of current methods of analysis. The data on the first analysis of the industrial chrome-ore standard give some indication of the precision to be expected in careful chrome ore analysis. The data are reproduced in table 1.

The data in the first column indicate the precision that might be expected in the careful analysis of a sample by one analyst using one of the conventional methods. The data in the second column indicate the effect of individual differences in the practice of these procedures. Both support Lundell's statement (1933) concerning the difficulty of keeping errors below 1 part in 100 in the analysis of natural materials.

TABLE 1.—*Precision of conventional methods of analysis*

[Data from Hartford, 1953]

	Percent deviation from mean	
	One analyst (multiple deter- minations on a single sample)	Ten laboratories (several different methods)
Cr ₂ O ₃ -----	0. 3	0. 5
Fe (total)-----	1. 0	3. 8
SiO ₂ -----	3. 0	3. 6
Al ₂ O ₃ -----	2. 5	5. 2
MgO-----	1. 2	7. 9

It is difficult, in the light of these results, to understand the convention that requires that the results of an analysis be expressed to two decimal places at all times. Some case might be made for its continued use in industry where arbitrary numbers arrived at by arbitrary procedures have a dollars and cents significance. In geochemical work, however, continued practice of this convention can be misleading. For example, expressing the result of an analysis for Al₂O₃ in chromite as 29.84 percent implies that the analyst is confident of his result to better than 1 part in 1,000. This would be presumptuous. Some question could be raised as to whether the result could justifiably be expressed as even 29.8 percent. This would imply a precision greater than 1 part in 100. When Al₂O₃ is calculated by difference a more realistic expression of this result would be as 30 percent. This would imply a precision no greater than 3 parts in 100,

and would more nearly present the facts concerning this method for the determination of Al_2O_3 in chromite.

The expression of the results of an analysis with a significance greater than that indicated by the data in table 1 should be reserved for those cases where greater significance is justified, that is, where unusually precise methods have been used.

The data in table 1 were available at the start of the U. S. Geological Survey program aimed at speeding up the analysis of chromite. Considering the success of the colorimetric methods used in the rapid methods for silicate-rock analysis, it was felt that a good possibility also existed for the use of the more rapid methods in chromite analysis. A precision of 2 parts per 100 is not unusual for good colorimetric methods.

The acceptance of the use of colorimetric procedures for the determination of major constituents has lagged for several reasons. Conventionally, colorimetric procedures have usually been used for the determination of only trace and minor constituents. A popular fallacy has arisen that working with dilute solutions "multiplies the error" of a determination. It can be shown, however, that the error involved in the proper use of a pipet for taking aliquots can be held to 1 part in 1,000. The error involved in making measurements of the light transmission of a color can be held to at least 1 part in 100 with normal methods; with special techniques (Hiskey, 1949) the error can approach 1 part in 1,000 or better. The error involved in the combined operation in taking an aliquot and measuring light transmission is additive and can easily be held to 1 part in 100.

It is usually the variables involved in the development of a color that govern the error involved in a colorimetric procedure. If the variables are known and can be controlled the errors should be no larger than those involved in other chemical operations, such as chemical separations.

ACKNOWLEDGMENTS

W. H. Hartford, Solvay Process Division, Allied Chemical and Dye Corp., provided the samples that were used for comparative analyses, and H. A. Heiligman and H. Montague, E. J. Lavino and Company, made available their methods of analyses of chromite.

SPECIAL EQUIPMENT

The procedures described here are based upon the use of several items of equipment which may not be available in most rock-analysis laboratories. They are a set of zirconium metal crucibles, a mercury cathode apparatus, and a spectrophotometer.

ZIRCONIUM CRUCIBLES

A set of a dozen hot-drawn zirconium metal crucibles, 25-ml (milli-liter) capacity, are used for the sodium peroxide fusions. As few as two crucibles will suffice. The crucibles, however, are among those items of equipment whose quantity will determine the number of samples that can conveniently be handled in one series.

The use of zirconium crucibles for sodium peroxide fusions has been advocated by Petretic (1951) and Young and Strachan (1953). Experience in the rapid-analysis laboratory has verified their findings. The crucibles used here were hot-drawn and made from metal manufactured by the Kroll process. The average loss of weight of a crucible after each fusion was 15–20 mg (milligram). One crucible has been in use for more than a year and has been subjected to more than 100 fusions. It is still in good condition.

The cost of commercial zirconium crucibles at the present time is about 15 times that of a comparable nickel crucible. Indications are however, that the useful life of the zirconium will be about 50 times that of the nickel crucibles. The savings in time and labor, which the zirconium crucibles afford, reduce their end cost still further.

Both nickel and platinum crucibles were used in the early phase of this work and schemes involving the use of each of the crucible materials have been developed. The use of each of these alternative materials, however, has numerous disadvantages.

If platinum crucibles are used the temperature of the sodium peroxide fusion must be carefully controlled to $480 \pm 20^\circ \text{C}$ (Rafter, 1950). This temperature is not sufficient to melt the sodium peroxide; instead it produces a sinter. The sample must be finely ground and must be thoroughly mixed with the sodium peroxide for sufficient reaction to take place. With some samples decomposition is not complete and the undecomposed sample must be separated and reprocessed. The sodium peroxide must be fresh and dry.

Another disadvantage is that iron has a significant solubility in hot platinum. A significant amount of the iron in a sample becomes dissolved during each heating. This must be recovered by leaching with hydrochloric acid and processed separately. As the determination of iron in chromite is relatively important it is preferable in this case to use a separate sample for the iron determination.

Nickel crucibles can be depended on for only 2 fusions. A considerable amount of the nickel is dissolved with each fusion and this amount varies widely. This provides another variable which must be controlled. Moreover, nickelic hydroxide dissolves only with great difficulty in the perchloric (or sulfuric) acid concentrations which the method allows. In a number of cases the hydroxide does not dissolve.

MERCURY CATHODE APPARATUS

A mercury cathode apparatus is used for the separation of chromium and iron from the chromite solutions. Several forms of such apparatus are commercially available. However, it has been found convenient and less expensive to use a 4-stage apparatus constructed from commercially available components. The essential items of a 2-stage unit (fig. 6) are a battery charger (6 volt) to provide a source of direct

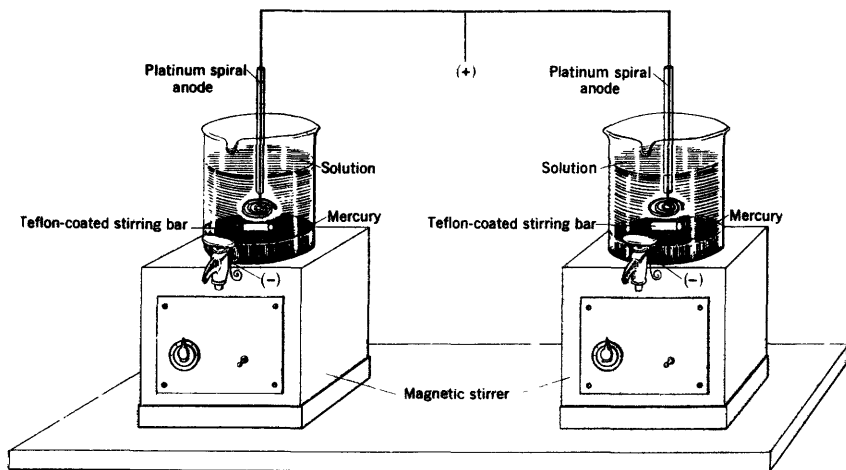


FIGURE 6.—Mercury cathode apparatus.

current, 2 platinum anodes, 2 magnetic stirrers with Teflon-coated stirring bars, and 2 electrolysis vessels.

SPECTROPHOTOMETER

A Beckman model B spectrophotometer is in use in the rapid-analysis laboratory for chromite analyses. The method can be adapted for the use of other spectrophotometers.

A photomultiplier attachment no. 4600 is used as the sensing element. The phototube voltage switch contained in the unit makes it possible to increase the sensitivity and to use narrower slit and band widths for blank and standard solutions having high absorbances.

A readily demountable carrier holding rectangular absorption cells with a path length of 50 mm (millimeter) is used for all absorbance measurements. A diagram of the holder is shown in figure 7. The holder now in use in this laboratory was constructed from bakelite. A holder made from 2 sheets of cardboard has been used successfully for many months, however.

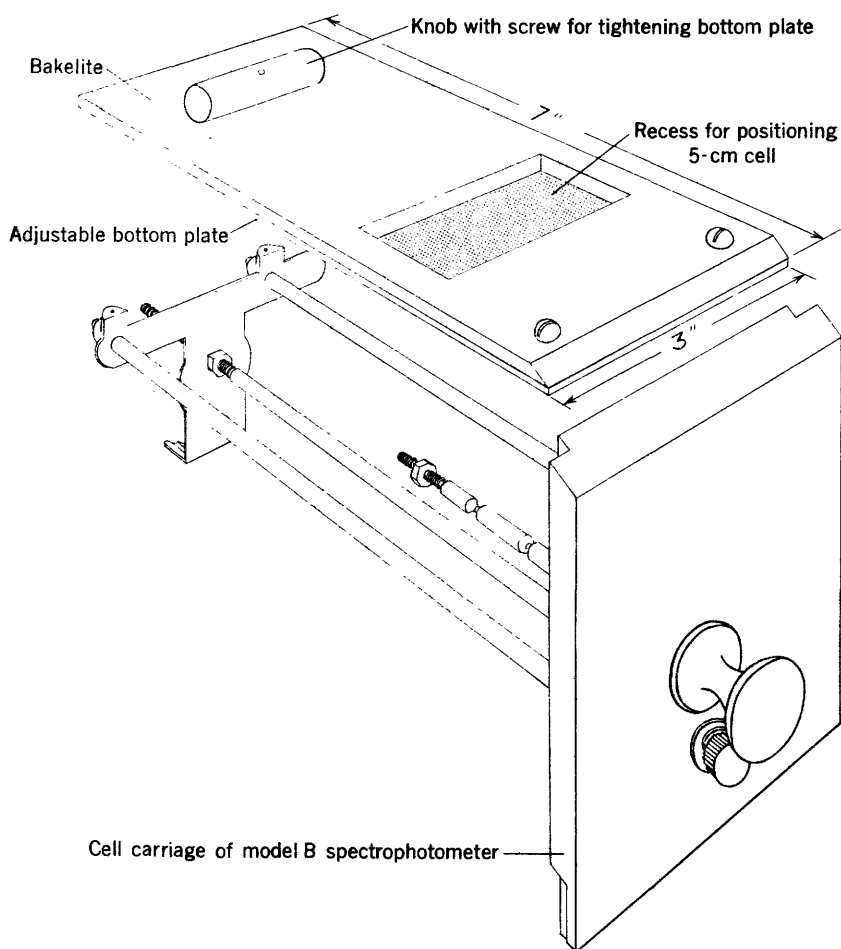


FIGURE 7.—Absorption cell holder for 5-cm rectangular cells. (Cell holder rests directly on carriage.)

AUTOMATIC PHOTOMETRIC TITRATION APPARATUS

The photometric titration apparatus used for the determination of magnesium and calcium is the same as that described by Shapiro and Brannock (1955, 1956).

PREPARATION OF SAMPLE SOLUTIONS

Most of the limited number of methods available for the effective decomposition of chromite have been either considered or tried in the development of these methods (Harpham, 1955; Reelfs, 1956).

Acid decomposition of chromite leaves silica in an insoluble form. It would be almost mandatory to determine silica in these solutions by volatilization with hydrofluoric acid. The action of perchloric

acid or a mixture of perchloric and sulfuric acids on chromite is relatively slow; solutions are best left "cooking" overnight. It also requires that the ore be finally ground.

Satisfactory schemes for the complete analysis of chromite using a perchloric acid decomposition can be developed, however, and may have some advantages for some samples. Perchloric acid is here recommended for the preparation of samples for the determination of calcium.

The use of phosphoric acid has an additional disadvantage. The high concentration of phosphate complicates many of the individual determinations of the elements.

Among the fluxes available for use, none seemed to provide the advantages afforded by sodium peroxide. Fusion with sodium or potassium bisulfate usually requires a prolonged heating period and does not attack some types of ores; the sample must be very finely ground. Silica is rendered insoluble. A mixture of sodium carbonate and potassium nitrate does not usually give a complete decomposition of a chromite sample. A mixture of sodium carbonate and sodium borate is only slightly better.

SOLUTION A

Solution A is the principal solution used in the analysis. The determinations of most of the elements are dependent upon the proper preparation of this solution.

Sodium peroxide is commercially available in several degrees of fineness. The various grades are usually described as "granular," "pellets," or "calorific" grade. Some manufacturers provide the sieve sizes of their products. The grades labeled "calorific," 30 mesh or 72 mesh, have been found to be best for the decomposition of samples of chromite.

A thorough mixture of the chromite sample with the sodium peroxide is important. Fine grains of sodium peroxide seem to provide a greater adsorptive surface area and are better able to keep the grains of sample suspended in the mixture. Coarse grains of peroxide allow a significant amount of the sample to remain as an undispersed clump. Fusion of a poorly mixed sample usually results in a significant amount of the sample being undecomposed.

As sodium peroxide is quite hygroscopic, specification of an arbitrary weight of reagent is impractical. Adequate control over the quantity of reagent can be obtained by using a volume dispenser. A scoop or cup fashioned from a plastic bottle cap cemented to a strip of polyethylene sheeting as a handle has been found to be adequate for this purpose. The volume of the cup should be sufficient to provide approximately 5 g (gram) of reagent.

Fusions in this laboratory are made over an open flame. The duration of heating of the fused melt is relatively important. The amount of zirconium dissolved is a function of time as well as temperature. Heating the peroxide mix for 5 minutes after it has become molten has been found to be an adequate compromise. It provides sufficient time for the decomposition of the sample and dissolves only a relatively small amount (15–25 mg) of zirconium.

It is specified that only 50 ml of water is to be added to the cooled melt and that the slurry is to sit for about 1 hour. The amount of hydrogen peroxide which remains in solution depends upon the alkalinity and the temperature of the solution; 50 ml of water has been arbitrarily selected because it produces a combination of alkalinity and temperature which releases most of the hydrogen peroxide from solution. One hour provides sufficient time for this evolution to proceed at room temperature. The acid solution cannot be heated for prolonged periods because of the formation of silicic acid. If much peroxide remains in solution it has been found impossible to effect a good separation during electrolysis on the mercury cathode. It also introduces an additional variable into most of the procedures.

Polyethylene beakers have been specified for the alkaline solutions in order to eliminate the introduction of SiO_2 into the solutions. The SiO_2 concentrations of cleaned chromite is usually 0.1–0.5 percent. The attack of hot alkaline solutions on glass containers may introduce relatively large concentrations of silica into solution and cause appreciable error. Preparation of a blank under similar conditions may not be adequate to eliminate this error.

Perchloric acid is specified for this work. Sulfuric acid can be used for most of the procedures but has a disadvantage when used with perchloric acid in the preparation of solution *C*. A fuming mixture of sulfuric and perchloric acids forms anhydrous perchloric acid which is relatively unstable and frequently results in minor explosions which, besides being rather unnerving and hazardous, may result in the loss of a significant amount of the sample.

The time necessary to obtain clear and complete solutions after acidification seems to vary with the iron concentration. Samples containing as much as 15 percent FeO dissolve completely in about 30 minutes; samples containing 20 percent FeO require several hours; a sample containing as much as 25 percent FeO requires about 20 hours (overnight). Samples containing more than 25 percent FeO may not dissolve completely in the specified acid concentrations in a practical amount of time. For such samples it has been found useful to substitute the following acidification procedure:

After the peroxide has been evolved, the alkaline slurries are washed into 200-ml plastic bottles. They are then centrifuged for

about 5 minutes at 1,500 rpm. The clear liquors are then decanted into plastic beakers and set aside. The sediments are dissolved with heating in the 25 ml of perchloric acid allowed. This acid solution, containing almost all of the iron, is diluted to approximately 500 ml with water and cooled. The alkaline liquor is then poured into this acid solution with stirring. A clear solution then results. As most of the silica remains in the alkaline liquor the solution can be used for the determination of silica with the introduction of very little error.

REAGENTS

Na_2O_2 , solid 32 mesh or finer.

HClO_4 , 70–72 percent

HF , 48 percent.

HCl , concentrated.

PROCEDURE

1. Transfer 0.400 g of sample (30 mesh or finer) to a zirconium crucible.
2. Add approximately 5 g of Na_2O_2 to the crucible by means of a small plastic scoop. Mix thoroughly with a platinum rod.
3. Heat the crucible over a low gas flame to the fusion temperature; keep molten, at dull redness, with occasional swirling, for 5 minutes.
4. Remove the crucible from the heat and allow the melt to cool.
5. Place the crucible into a 100-ml polyethylene beaker.
6. Add 50 ml of water directly into the crucible and cover the beaker immediately with a plastic cover.
7. When the reaction has ceased (5–15 min), rinse the crucible and lid and scrub with a rubber policeman, catching the rinsings in the plastic beaker.
8. Wait at least 1 hour for the hydrogen peroxide to be evolved before proceeding with the next step.
9. Transfer the contents of the plastic beaker with stirring to a 800-ml Pyrex beaker containing 500 ml of water and 25 ml of HClO_4 . Pour a portion of the acid solution back into the plastic beaker and allow it to dissolve the adhering film of precipitated hydroxides.
10. Rinse the plastic beaker with water, catching the rinsings in the glass beaker.
11. Allow the solutions to sit until clear (15 min to overnight)
12. Transfer the solution to a 1-liter volumetric flask. When at room temperature dilute to 1 liter with water and mix well.

SOLUTION B

PROCEDURE

The following operations are conveniently performed in groups of 4 samples each.

1. Transfer 100 ml of solution A to the electrolysis vessel of the mercury cathode apparatus.
2. Dilute with water to approximately 200 ml.
3. Add 2 ml of perchloric acid and approximately 15 ml of clean mercury
4. Electrolyze at approximately 10 amp (5 volts) for at least 30 minutes.
5. Drain the mercury from the electrolysis vessel while the current is still on.
6. Transfer the electrolyzed solution to a 600-ml beaker and rinse the electrolysis vessel with water.

7. Transfer the solution to a 500-ml volumetric flask. When at room temperature dilute to 500 ml with water, and mix well.

SOLUTION C

The volatilization of chromium as CrO_2Cl_2 with concentrated HCl is a well-known operation (Hillebrand and others, 1953, p. 526). The volatilization of chromium as CrO_2F_2 using concentrated HF is not well known. In the following procedure most of the chromium and all of the silica is volatilized using HF . The remainder of the chromium is volatilized with HCl .

Chromium volatilizes only in the oxidized state. The treatment with halide causes a partial reduction. The reduced chromium must be reoxidized before the treatment with further amounts of halide becomes effective.

Fuming the solutions should be continued even after the complete volatilization of the chromium is indicated in order to ensure the complete oxidation of the vanadium, nickel, and iron remaining in solution.

PROCEDURE

1. Transfer 200 ml of solution A to a 250-ml beaker using a graduated cylinder.
2. Add 15 ml of HClO_4 (72 percent).
3. Evaporate the solution on a hot plate or a steam bath until only the concentrated acid and salts remain.
4. Transfer the solution to a large platinum dish using a minimum amount of water for rinsing.
5. Evaporate the solution to strong fumes of HClO_4 .
6. While fuming add 5 ml of concentrated HF . Continue fuming until the orange color of dichromate reappears.
7. Alternate the addition of HF and fuming several times until almost all the chromium has been volatilized.
8. Allow the solution to cool and transfer the contents of the dish to the original 250-ml beaker.
9. Heat the solution to fumes of HClO_4 . Cover the beaker with a watch glass and continue heating. If the solution is tinted green a considerable amount of Cr(III) may be present. After oxidation to Cr(VI) this should be volatilized by the addition of 2 ml of HCl (conc.). The cycle should be repeated if necessary. Fuming should be continued for at least 15 minutes.
10. Allow the solution to cool. Dilute to approximately 50 ml with water.
11. Transfer the solution to a 100-ml volumetric flask, dilute to mark, and mix well.

PROCEDURES FOR THE DETERMINATION OF THE INDIVIDUAL CONSTITUENTS

At least two standard samples and reagent blank solution are included in each series of determinations. National Bureau of Standards standard sample no. 103, chrome refractory was used as the reference standard in this laboratory. The metallurgical chrome-ore standard, Andrew McCreath and Sons (Hartford, 1953), was used as an auxiliary standard.

Unless otherwise specified, the operation described for each step in a procedure should be completed for all the samples in a series before proceeding to the next step.

Cr_2O_3

The procedure described here for the determination of Cr_2O_3 in chromite is almost exactly the same as that recommended by Bryant and Hardwick (1950). It is described again here so as to make this account of the analysis of chromite more complete.

The basic volumetric procedure for the determination of Cr_2O_3 has been used for many years (Cunningham and McNeill, 1929) and many variations of the procedure are used by industrial laboratories (Hartford, 1953). The particular modification used here has been chosen because it is among the most simple and reliable.

Several attempts to determine Cr_2O_3 by differential colorimetry (Hiskey, 1949) have been made in the rapid-analysis laboratory. Although differential colorimetry has been successfully applied to solutions of potassium dichromate (Bastian and others, 1950), attempts to apply the method to chromite solutions have not been successful. Control of the variables, acidity, oxidation state of chromium, and interfering cations have been insufficient to give an adequate precision.

Work with alkaline solutions of chromate has not been attempted although better control of several variables might be obtained by this means.

The volumetric determination of Cr_2O_3 is so rapid and trouble free, however, that it is doubtful whether substitution of a colorimetric procedure would make a substantial saving in time and precision.

A water-repellant coated pipet and burette add measurably to the speed of this determination without sacrificing precision.

In this laboratory two determinations are usually made for Cr_2O_3 . One determination is performed on an aliquot of solution A, the other on a separate portion of sample by the conventional method. The conventional method is also used on those samples for which the determination of Cr_2O_3 is the only determination requested.

The results for Cr_2O_3 by this method are usually 1 percent low when compared with $\text{K}_2\text{Cr}_2\text{O}_7$ taken as the primary standard. The cause of the low results is not known. For greater accuracy it is advisable that a correction factor be used based on the analysis of Bureau of Standards chrome refractory and the Metallurgical chrome-ore standard.

REAGENTS

Standard dichromate solution: 0.1 N.

H₂SO₄: 1+1.

Indicator solution: Dissolve 0.2 g of sodium diphenylamine sulfonate in 100 ml of water. Add this solution to 900 ml of a cooled solution of 1+1 phosphoric acid.

Mohr's salt solution, Fe(NH₄)₂(SO₄)₂·6H₂O: Dissolve 150 g of ferrous ammonium sulfate in a solution containing 1 liter of water and 350 ml of 1+1 H₂SO₄. Dilute to 4 liters.

HNO₃: Concentrated.

KMnO₄: 0.1 N.

HCl: 1+1.

PROCEDURE (Cr₂O₃ in separate sample)

1. To an iron, nickel, porcelain, or zirconium crucible, add approximately 5 g of Na₂O₂ with a scoop.
2. Transfer 0.500 g of sample to the crucible.
3. Mix thoroughly with a platinum rod cover and with a suitable lid.
4. Heat the sample over a low flame and keep molten at dull redness, with occasional swirling, for 5 minutes.
5. Allow the crucible and contents to cool.
6. Place the crucible in a 800-ml Pyrex beaker.
7. Add 200 ml of water.
8. After the reaction has ceased (10–15 min), insert a glass boiling rod and boil the solution for 10 minutes.
9. If an iron, nickel, or zirconium crucible has been used, scrub it well with a rubber policeman, rinse, and remove it from the beaker.
10. Add 50 ml of 1+1 H₂SO₄ and 5 ml of HNO₃.
11. Warm to dissolve any precipitate.
12. Dilute to approximately 500 ml. If a porcelain crucible and lid were used, rinse and remove them at this point. Add 2 ml of permanganate solution and boil the solution for 10 minutes.
13. Add 10 ml of 1+1 HCl and continue boiling for 15 minutes.
14. Allow the solution to cool to room temperature.
15. Add 25 ml of indicator solution. By pipet add 50 ml increments of Mohr's salt solution until an excess is present (indicated by the disappearance of the purple oxidized phase of the indicator) and back titrate with the standard dichromate solution.

CALCULATION OF PERCENT Cr₂O₃

Standardize the Mohr's salt solution against the standard dichromate solution.

The dichromate equivalent of Mohr's salt solution added minus the back titration equals the dichromate solution equivalent of the sample.

$$\text{Percent Cr}_2\text{O}_3 = \frac{\text{ml dichromate} \times 2.534 + 100}{\text{sample wt (mg)}}$$

PROCEDURE (Cr₂O₃ in solution A)

1. Transfer 500 ml of solution A to a 1-liter beaker using a clean, calibrated 500-ml volumetric flask. Prerinse the flask with each sample solution before the transfer. Rinse the flask well with water after each transfer, catching the rinsings in the beakers.
2. Add 50 ml of 1+1 H₂SO₄ to each beaker.
3. Place a glass boiling rod in each solution.
4. Bring the solutions to a boil on a hot plate.
5. Add 2 ml of KMnO₄ to each beaker and continue the steps described above (steps 12–15).

TOTAL IRON AS FeO

The total iron content of a chromite ore is important in establishing the ratio of Cr to Fe and the consequent quality and price of the ore. As Cr_2O_3 can be routinely determined with a precision of about 1 part in 500 it would also be desirable to obtain this precision in the determination of iron. For this reason, a more precise differential spectrophotometric method is here used for this determination. The differential procedure described here is not, however, the rigorous technique that affords a precision of 1 part in 1,000 or better (Hiskey, 1949). It affords a precision of only one part in several hundred. If a greater precision is required it is advisable that light transmission measurements be made by the more rigorous technique on a spectrophotometer known to afford a high degree of precision (Hiskey and others, 1950).

Estimation of the percent FeO can be made by graphical comparison of the absorbance of the solution to the absorbance of standard iron solutions, or by interpolation.

The use of 1,10-phenanthroline for the determination of iron has been very critically evaluated (Fortune and Mellon, 1938) and is among the most trouble-free of the procedures described here.

Iron must be in the reduced state, hence, the emphasis on waiting at least 15 minutes after the addition of the hydroxylamine hydrochloride solution. If sufficient time for reduction has been allowed, light absorbance measurements can be made immediately after the final dilution of the samples.

The colored solutions are stable for at least several months and standard solutions can be saved and reused as convenient.

REAGENTS

Hydroxylamine hydrochloride, 10 percent: Prepare 500 ml.

Orthophenanthroline solution, 0.1 percent: Prepare 1 liter.

Sodium citrate buffer solution, 10 percent: Prepare 1 liter.

Iron wire, A. C. S.

HCl, 1+1.

Standard iron solution: Dissolve 0.800 g of iron wire with 25 ml. of 1+1 HCl in a 1,000-ml volumetric flask. Allow to cool and dilute to 1,000 ml with water and mix well (stock solution). Transfer 25 ml of the stock solution to a 500-ml volumetric flask, dilute to the mark with water and mix well. Each milliliter of this solution contains 0.04 mg Fe and is equivalent to 2.00 percent Fe (2.57 percent FeO) in a solution of a sample prepared as described under "Preparation of sample solutions, solution A."

PROCEDURE

1. To a series of 250-ml volumetric flasks add 5, 6, 7, 8, 9, 10, 11, and 12 ml of the standard iron solution to the first 8 flasks, respectively. (Use a calibrated 10-ml graduated pipet and a 5- and 10-ml calibrated volumetric pipet.) Transfer 5 ml of solution A of the 2 standard chromite samples to the next 2 flasks. Transfer 5 ml of solution A of the samples being analyzed to the remaining flasks.

2. Add 50–60 ml of water.
3. Add 5 ml of hydroxylamine hydrochloride solution.
4. Allow to stand for 15 minutes.
5. Add 20 ml of orthophenanthroline solution.
6. Add 20 ml of citrate buffer solution.
7. Dilute to 250 ml with water.
8. Mix the solutions well.
9. For chromite estimated to contain less than 25 percent FeO use the first standard iron solution (12.87 percent FeO) as a reference blank. For chromite estimated to contain more than 25 percent FeO use the solution containing 10 ml of standard iron solution (25.74 percent FeO) as a reference blank. Determine the absorbance of the sample solution against the appropriate reference blank, at 510 m μ (millimicron), using absorption cells with 5-cm (centimeter) light path.

CALCULATION OF PERCENT IRON

Calculate the percent iron by interpolation of the absorbance of the sample between the absorbances of the two standard iron solutions falling above and below the absorbance of the unknown. Check the standardization of the standard iron solutions by calculating the percent iron in the solutions of the two standard chromite samples. If the need for a correction is indicated calculate a correction factor by dividing the certified percent FeO in the standard chromite sample by the calculated percent FeO. Multiply the calculated percent FeO in the samples by the correction factor to find the corrected percent FeO.

SiO₂

The use of the reduced silico-molybdate color for the determination of SiO₂ has also been critically evaluated (Boltz and Mellon, 1947; Bunting, 1944; Carlson and Banks, 1952) and is very reliable. The colored solutions are stable for long periods of time and can be saved for rechecking purposes as convenient.

In "purified" chromite silica concentrations are 0.3–1.0 percent. The analyst may be tempted to take a larger aliquot in order to increase the sensitivity. Acid concentration and other conditions are, however, quite critical in this procedure. A larger aliquot increases the acidity and changes the conditions and may prevent full development of the color.

REAGENTS

Ammonium molybdate reagent solution: Dissolve 7.5 g of ammonium molybdate in 75 ml of water. Add 10 ml of 1+1 H₂SO₄ and dilute to 100 ml. Store in a plastic bottle. Prepare fresh each week.

Tartaric acid solution, 10 percent: Prepare 500 ml and store in a plastic bottle.

Reducing solution: Dissolve 0.70 g of sodium sulfite (Na₂SO₃) in 10 ml of water.

Add 0.15 g of 1-amino-2-naphthol-4-sulfonic acid and stir until dissolved.

Dissolve 9 g of sodium bisulfite in 90 ml of water and add to the solution above and mix. Store in a plastic bottle in a cool place. Prepare fresh every other day.

PROCEDURE

1. Using a pipet, transfer 5 ml of solution A to a 100-ml volumetric flask.
2. Add 5 ml of water to each flask.
3. Add 1 ml of ammonium molybdate solution with an automatic pipet, swirling the flask during the addition.

4. Allow the solutions to stand 10 minutes.
5. Add 4 ml of tartaric acid solution with an automatic pipet, swirling the flasks while adding. Mix well.
6. Add 2 ml of the reducing solution with an automatic pipet while swirling the flasks.
7. Dilute the flasks to 100 ml with water.
8. Mix well.
9. Allow the solutions to stand at least 30 minutes.
10. Using the absorption cell with 5-cm path length determine the absorbance of each solution at $650\text{ m}\mu$ using a reagent blank solution as the reference.

CALCULATION OF PERCENT SiO_2

Determine the absorbance factor of the SiO_2 in a standard sample carried along in the series by dividing the percent SiO_2 by the absorbance. Multiply the absorbance of the sample solution by the factor to find the percent SiO_2 in the sample.

Al_2O_3

Hillebrand and others (1953, p. 494) have characterized the determination of alumina in rocks and minerals as being "one of the analyst's most difficult problems." The conventional procedures for the determination of alumina in chromite usually give results which support this statement. The results are frequently unreliable; the procedures are involved and time consuming.

Although the spectrophotometric procedure described here is rapid and compares favorably with other methods for the determination of alumina, a considerable area for improvement still remains. The procedure is direct, however, and makes the determination of alumina independent of the other determinations. It gives results of equal uncertainty in much less time than is required by the conventional procedures.

Most colorimetric reagents used for the determination of alumina yield highly absorbing blank solutions. This is frequently a source of error. Most of the reagents form complexes that give apparent conformity to the absorption law over restricted ranges. This greatly limits their usefulness.

Among the various titrimetric and colorimetric procedures investigated in the rapid-analysis laboratory, the procedure using alizarin red-S has seemed to be the best of those tried thus far. Improved methods for the determination of alumina are, however, subjects of frequent investigation in this laboratory.

Zirconium can cause serious interference in the alizarin procedures if its effect is not somehow counteracted. A considerable quantity of zirconium enters the solutions following fusions in zirconium crucibles. After some investigation, however, it was found that the effects of zirconium could be easily counteracted by adding small amounts of phosphate ion to the solutions just prior to the addition of alizarin. Zirconium phosphate forms a tightly bound complex

that is usually not present in sufficient quantity to form a visible precipitate and shows no evidence of otherwise interfering with the determination of alumina.

The use of the calcium-aluminum alizarin complex for the determination of alumina has been critically described by Parker and Goddard (1950).

REAGENTS

Standard alumina solution: Dissolve 0.212 g of aluminum metal with 25 ml of 1+1 HCl and dilute the solution to 1 liter with water (stock solution). Transfer 25 ml of the stock solution to a 500-ml volumetric flask and dilute the solution to 500 ml with water. Five milliliters of this solution is equivalent to a solution of a sample containing 25 percent Al_2O_3 prepared as described under "Preparation of sample solutions, solution B."

Calcium chloride reagent solution: Slowly add 1+1 HCl to a slurry containing 65 g CaCO_3 in 300 ml of water until the CaCO_3 is completely dissolved. Boil the solution for several minutes. Cool and dilute to 500 ml (stock solution). Dilute 10 ml of the stock solution with water to 500 ml to prepare the reagent solution containing 1 mg Ca per milliliter.

Buffer solution: 280 g of sodium acetate and 120 ml of acetic acid diluted to 2 liters with water.

Potassium dihydrogen phosphate solution, 1.92 grams per liter: 1 ml = 1 mg P_2O_5 . Alizarin red-S solution, 0.1 percent: Prepare 500 ml.

PROCEDURE

Prepare at least three reagent blank solutions with each series of determinations.

With high alumina samples containing 20–30 percent Al_2O_3 check for the conformity of the solutions to the absorption law with each series. Prepare standards corresponding to 5, 10, 15, 20, 25, and 30 percent Al_2O_3 by pipetting 1, 2, 3, 4, 5, and 6 ml of standard alumina solution, respectively, into 100-ml flasks. Plot absorbances versus percent Al_2O_3 on graph paper. If nonconformity to the absorption law is indicated at the high concentrations of Al_2O_3 , use the graph to calculate the percent Al_2O_3 for those solutions.

1. Carefully transfer 5 ml of solution B to a 100-ml volumetric flask, using a pipet.

2. With a pipet, add 5 ml of the CaCl_2 solution to each flask and mix.

3. Using a graduate, add 10 ml of the acetate buffer solution and mix well.

4. Allow the solutions to stand at least 10 minutes.

5. Add 2 ml of the phosphate solution and mix.

6. Add approximately 50 ml of water.

7. Carefully add 5 ml of the alizarin solution, with a pipet.

8. Dilute the solution to 100 ml with water.

9. Mix the solutions well.

10. In the 5-cm path length absorption cells, determine the absorbance of each reagent blank solution against the other at 485 m μ . They should vary no more than 0.01 absorbance unit.

11. Determine the absorbance of the aluminum-alizarin solutions against the absorbance of the reagent blank solution.

CALCULATION OF PERCENT Al_2O_3

Samples with Al_2O_3 concentrations < 20 percent.—The absorbances of solutions of these samples usually fall in the linear portion of the graph. Calculate the absorbance factor using the absorbance of the 20 percent standard solution (4 ml of standard alumina solution). Multiply absorbances of the sample solu-

tions falling in the linear portions of the graph by the factor to calculate their percent Al_2O_3 .

Samples with Al_2O_3 concentrations >20 percent.—The absorbances of solutions of these samples usually fall in curved portions of the plotted line. The percent Al_2O_3 in these samples should be read directly from the graph.

TiO₂

Yoe and Armstrong (1947) have described the use of Tiron (disodium-1,2-dihydroxybenzene-3,5-disulfonate) for the spectrophotometric determination of titania. Chromium (III), vanadium (IV), mercury (I), and iron (III) ions are possible interferences which may be present in significant concentrations. Mercury cathode electrolysis quantitatively separates chromium and iron present in the solution. The continued use of sodium dithionite is recommended in order to detect and correct occasional incomplete separations. A significant change in absorbance after the addition of dithionite indicates that iron and possibly chromium have not been separated completely. Interference from significant quantities of vanadium should be corrected by preparing blank solutions containing the appropriate amounts of vanadium. Approximately 0.1 percent V_2O_5 in the sample can be tolerated without causing a significant error in the determination of 0.3 percent TiO_2 .

REAGENTS

Tiron (disodium-1,2-dihydroxybenzene-3,5-disulfonate): Dry reagent powder.

Buffer solution: 80 g of ammonium acetate and 30 ml of glacial acetic acid diluted to 2 liters with water.

Sodium dithionite, $\text{Na}_2\text{S}_2\text{O}_4$: Dry reagent powder.

PROCEDURE

1. To the first of a series of 150-ml beakers add 25 ml of solution *B* of a chromite standard; add 25 ml of solution *B* of the samples to the remaining beakers.

2. With a small scoop add approximately 100 mg of dry Tiron powder to the beaker and mix.

3. With a pipet add 50 ml of the buffer solution to the solution and mix.

4. Add approximately 10 mg of sodium dithionite powder to the beaker and mix gently. Read the absorbance between 1 and 5 minutes after adding dithionite.

5. Using the 5-cm path length absorption cells read the absorbances of the colored solutions against the absorbance of a reagent blank at 410 $\text{m}\mu$.

CALCULATION OF PERCENT TiO_2

Determine the absorbance factor of the TiO_2 in the standard sample. Multiply the absorbance of the sample solution by the factor to find the percent TiO_2 in the sample.

MgO

The procedure described here for the determination of MgO (Betz and Noll, 1950) is actually the determination of MgO plus CaO. When more than several tenths of a percent CaO is believed to be

present, a correction for CaO should be made after CaO has been determined.

Most of the chromite concentrates analyzed in the rapid-analysis laboratory were found to contain no more than several tenths of a percent CaO. In calculating the percent MgO in such samples very small or negligible corrections were necessary for the CaO content of the sample. In chrome ore, however, the CaO content may be significantly greater. Corrections are made on a molar basis; 1.00 percent CaO=0.72 percent MgO.

REAGENTS

Versene solution: Dissolve 20 g of disodium ethylenediamine tetraacetate in 20 liters of water and transfer to the Mariette bottle.

Buffer solution: Dissolve 66 g of NH_4Cl in 1 liter of 1+1 NH_4OH and store in a plastic bottle.

Indicator solution: Eriochrome Black-T solution, 0.2 percent. Prepare 50 ml. Store in a cool place, prepare fresh twice weekly.

Standard MgO solution: Dissolve 3.86 g of magnesium metal ribbon in 50 ml of 1+3 HCl and dilute to 1 liter (stock solution). Transfer 50 ml of the stock solution to a 1-liter volumetric flask and dilute with water to 1 liter. Ten milliliters of this solution contains 3.2 mg of MgO and is equivalent to a solution of a sample containing 30 percent MgO prepared as described under "Preparation of sample solutions, solution B."

PROCEDURE

1. To a series of 400-ml tall-form beakers add 10 ml of standard MgO solution to the first, 200 ml of the solution B reagent blank solution to the second, and 200 ml of solution B of the samples to the other beakers.

2. Add 1 ml of the standard MgO solution to each beaker.

3. Dilute the solution to approximately 250 ml.

4. Before the start of each titration, add 25 ml of buffer solution, 1 ml of the indicator solution, and a magnetic stirring bar to the beaker. Titrate the solution with the automatic photometric titration apparatus to well past the indicated end point, at 670 $\text{m}\mu$.

CALCULATION OF PERCENT MgO

1. Compute the total seconds taken for the titration.

2. Subtract the seconds taken for the titration of the reagent blank solution from the titration of the sample solution.

3. Calculate the titration factor by dividing 20.0 percent MgO by the net seconds taken for the titration of the standard solution.

4. Multiply the net seconds taken for the titration of the sample solution by the titration factor to determine the percent MgO in the sample.

ALTERNATIVE PROCEDURE

It may in many cases be impractical or inconvenient to set up apparatus for the spectrophotometric titration of the alkaline earths. It may be more practical to employ a visual titration procedure such as that developed by Leonard Shapiro of this laboratory. An aliquot of solution B is titrated with standard Versene solution (2.1 g per liter) using 2 ml of a mixed indicator solution to detect the end point. The indicator solution consists of 100 mg eriochrome black-T and 20 mg of methyl red diluted to 100 ml. The titration is continued until the disappear-

ance of the red color. The end point is, however, very difficult to detect in the presence of aluminum. Aluminum should be separated by an ammonia precipitation or otherwise, before the start of the titration.

V_2O_5

Vanadium must be in the pentavalent state for its determination as the phosphotungstovanadate (Cooper and Winter, 1949; Wright and Mellon, 1937).

REAGENTS

Mixed reagent: Mix together 200 ml of 1+1 HNO_3 and 100 ml of 3+2 H_3PO_4 .

Dilute to 400 ml with water. Add 100 ml of 0.2 M Na_2WO_4 and mix.

Standard vanadium solution: Dissolve 100 mg of V_2O_5 in a polyethylene beaker containing a warm solution of 15 g of NaOH dissolved in 50 ml of H_2O . Pour the alkaline solution into a 1-liter volumetric flask containing 25 ml of $HClO_4$ (conc.) in 500 ml of water. Dilute to 1 liter (stock solution). Dilute 10 ml of the stock solution to 250 ml. Ten milliliters of this solution contains the equivalent of 0.04 mg of V_2O_5 and is equivalent to the solution of a sample containing 0.1 percent V_2O_5 prepared as described under "Preparation of solutions, solution C."

PROCEDURE

1. To a series of 100-ml volumetric flasks add 10 ml of standard vanadium solution, and 40 ml of water to the first, 50 ml of the standard solution to the second and 50 ml of solution C to the other.
2. Add 25 ml of mixed reagent, and mix.
3. Allow the solutions to stand for 2 hours.
4. Add 1 ml of hydroxylamine hydrochloride (10 percent).
5. Dilute to 100 ml with water.
6. Mix the solutions well.
7. Wait about 10 minutes.
8. In the 5-cm path length absorption cells measure the absorbance of each of the solutions compared to a reagent blank at 410 $m\mu$.
9. Calculate the percent V_2O_5 in the sample by multiplying the absorbance by an absorbance factor calculated from the absorbance of the standard vanadium solution.

MnO

This procedure is based on a study by Leonard Shapiro of this laboratory. He found that manganese could be effectively oxidized to permanganate in dilute acid solution by allowing a solution to stand at room temperature for several hours with a mixture of silver nitrate and ammonium persulfate.

The usual procedure for the oxidation of manganese to permanganate (Cooper, 1953; Smith, 1950) depends upon the oxidation action of potassium periodate or ammonium persulfate in strong, hot sulfuric acid solution. This has been found to give unreliable results in routine use.

All traces of chlorides introduced during the volatilization of CrO_2Cl_2 should be removed by continued fuming with perchloric acid. If not removed, the cloud of silver chloride formed seriously interferes in the measurement of the permanganate color.

The maximum absorbance of the permanganate color occurs at 510 $m\mu$. Dichromate, however, also absorbs strongly at this wave length. At 550 $m\mu$ the absorbance of dichromate is reduced to about one-fifth while the permanganate absorbance is reduced about one-half. In order to reduce any interference from dichromate which may have avoided volatilization, 550 $m\mu$ has been chosen as the measuring wavelength in the procedure.

REAGENTS

Silver nitrate solution: 1 percent.

Ammonium persulfate: Dry powder.

Standard manganese solution: Dissolve 0.078 g of manganese metal in 25 ml of 1+1 $HClO_4$. Cool and dilute to 1 liter with water (stock solution). Dilute 10 ml of the stock solution to 250 ml. Ten milliliters of this solution contains 0.04 mg MnO and is equivalent to a solution of a sample containing 0.1 percent MnO prepared as described under "Preparation of sample solutions, solution C."

PROCEDURE

1. To a series of 150-ml beakers, add 20 ml of water to the first, 10 ml of standard manganese solution and 10 ml of water to the second, and 20 ml of solution C of the samples to the other beakers.

2. Add 25 ml of water by pipet.

3. Add 1 ml of silver nitrate solution.

4. Add 2 scoops of ammonium persulfate (0.5 g)

5. Allow to stand at least 1 hour.

6. In the 5-cm absorption cells, read the absorbance of the solution against a reagent blank at 550 $m\mu$.

7. Calculate the percent MnO by multiplying the absorbance of the solution by the absorbance factor determined on the standard solution.

NiO

The procedure used for the determination of NiO is based upon that described by Taylor (1956). The method was selected because of its sensitivity and reliability. The procedure can tolerate relatively large concentrations of Fe(III), Cr(VI) and alkali salts.

It is important in the procedure that Ni and Fe be thoroughly oxidized. This again emphasizes the importance of fuming the solution C thoroughly after the volatilization of chromium has been effected.

REAGENTS

Sodium citrate: 10 percent.

α -furildioxime: 1 percent in 50 percent ethanol.

Ammonium hydroxide: concentrated.

Chloroform.

Standard nickel solution: Dissolve 0.100 g of nickel metal in 15 ml of concentrated $HClO_4$. Heat to fumes of $HClO_4$ and maintain fuming temperature for 15 minutes. Dilute to 100 ml with water (stock solution). Dilute 10 ml of the stock solution to 100 ml with water. Each 0.1 ml of this solution contains 0.01 mg Ni and is equivalent to a solution of a sample containing 0.32 percent NiO as described under "Preparation of sample solutions, solution C."

PROCEDURE

1. To a series of 60-ml separatory funnels, transfer 5 ml of solution *C* of the reagent blank solution to the first, 0.1 ml of the standard nickel solution to the second, 0.2 ml of the standard nickel solution to the third, and 5 ml of solution *C* of the sample to the next.

2. Add approximately 20 ml of water.

3. Add 5 ml of the sodium citrate solution with an automatic pipet and mix the solution.

4. Add 0.1 ml of the α -furfildioxime solution. Wash down the sides of the funnel and mix the solution.

5. Add 0.5 ml of ammonium hydroxide and mix.

6. Add 10 ml of chloroform.

7. Shake the solutions vigorously for about 1 minute (200 shakes).

8. Collect the chloroform layer (lower) in a dry, clean, 50-ml volumetric flask.

9. Repeat the chloroform extractions two times, collecting the chloroform extracts in the 50-ml volumetric flask.

10. Dilute the flasks to the mark with chloroform.

11. Read the absorbances of the solutions at 435 $m\mu$ in the 5-cm path length absorption cells against the reagent blank solution.

CALCULATION OF PERCENT NiO

Determine the absorbance factor by dividing 0.32 percent NiO by the absorbance of the second flask (0.01 mg Ni); divide 0.64 percent NiO by the absorbance of the third flask (0.02 mg Ni). The absorbance factors should be within several percent of each other.

Multiply the absorbance of the solution by the average factor to find the percent NiO in the sample solution.

CaO

Sodium peroxide from a number of manufacturers was tested in the rapid-analysis laboratory and was found to contain significant amounts of calcium. The CaO content averaged 0.04 percent. The amount of calcium taken in with the amount of reagent usually used would represent about 0.5 percent CaO in a 0.4 g sample of chromite. This is well above the usual range of the CaO content of chromite. It would be difficult to blank out this quantity adequately by normal procedures for the determination of calcium. For this reason it is preferable to determine CaO on a separate sample without relying on sodium peroxide.

Calcium can also be determined in the solution resulting from step "13" by flame photometry if more convenient (Mosher and others, 1950).

REAGENTS

HClO₄, 72 percent.

NH₄Cl-methyl red solution: Add 10 ml of 0.05 percent methyl red solution to 1 liter of 15 percent NH₄Cl.

NH₄OH solution: 1+20 NH₄OH.

NH₄OH solution: 1+1 NH₄OH.

Wash solution: 2 percent NH₄Cl solution made slightly alkaline with NH₄OH
NaOH solution, 15 percent: Store in a plastic bottle.

Murexide solution, 0.2 percent: Prepare 50 ml. Do not store longer than 2 days.

Standard CaO solution: The calcium chloride reagent solution prepared for the determination of Al_2O_3 is used. One milliliter contains 1 mg CaO and is equivalent to a solution of a sample containing 0.2 percent CaO as prepared according to the procedure described below.

PROCEDURE

Carry along a reagent blank solution and a standard solution containing 5.0 mg CaO (1.0 percent CaO) in the series of samples.

1. Transfer 0.500 g of sample to a 250-ml Erlenmeyer flask.
2. Add 15 ml HClO_4 .
3. Heat to fumes of HClO_4 and continue heating until sample is completely dissolved (4 to 16 hours).
4. Cool, dilute to approximately 100 ml with water.
5. Electrolyze entire sample in the mercury cathode apparatus as described under "Preparation of sample solutions, solution B."
6. Transfer the electrolyzed solution to a 250-ml beaker and dilute to approximately 150 ml with water.
7. Add 25 ml of NH_4Cl methyl red solution.
8. Neutralize with NH_4OH until color changes to yellow.
9. Add 2 drops of 1+20 NH_4OH in excess.
10. Boil the solution for 2 minutes.
11. Allow the precipitate to settle 15 minutes.
12. Filter the solution through a moderately retentive filter paper into a 400-ml tall-form beaker.
13. Wash the precipitate with a dilute solution (2 percent) of ammonium chloride made slightly alkaline with ammonium hydroxide.
14. Adjust the pH to 12.0 with 15 percent NaOH solution and dilute the solution to approximately 250 ml with water.
15. Add 1 ml of standard CaO solution to the solution.
16. Add a plastic-coated stirring bar and 1 ml of murexide indicator to the solution.
17. Using the automatic titration assembly, titrate the solution at 590 $\text{m}\mu$ to well past the end point.

CALCULATION OF PERCENT CaO

1. Compute the total seconds taken for the titration.
2. Subtract the seconds taken for the titration of the reagent blank solution from the titration of the sample solution.
3. Calculate the titration factor by dividing 1.0 percent CaO by the net seconds taken for the titration of the standard solution.
4. Multiply the net seconds for the titration of the sample solution by the titration factor to determine the percent CaO in the solution.

H_2O

The total water content of the purified chromite from many different localities analyzed in this laboratory seldom exceeded more than several tenths of a percent. This and the mineralogical evidence available indicate that water is not an integral part of the chromite molecule. Where water is found in chromite it is almost always associated with the silicate impurities present; such samples usually contain relatively high concentrations of SiO_2 .

The water content of uncleaned chromite and chrome ore can be as much as several percent. The water content in such cases can have an important bearing on the summation of an analysis and the preparation of the sample for analysis.

It is a commonly accepted fact that finely ground samples adsorb greater amounts of moisture than do coarse samples. Hartford (1953, p. 291) has noted that such adsorbed moisture is not driven off by heating the sample to 110° C; a temperature of 230° C is necessary. In spite of this fact, however, many directions for the preparation of chromite standards and samples for analysis require that samples be dried at 110° C for several hours.

It would be preferable to prepare samples by drying at 230° C. It would be still better to conduct analyses on air-dried samples as recommended by Hillebrand and others (1953, p. 821) and to make separate determinations of water. Analyses could then be calculated on a water free basis if desired.

In the rapid-analysis laboratory, total water is determined by the Penfield tube method (Hillebrand and others, 1953, p. 827-828).

Serious objections have, however, been raised to the use of the Penfield method for the determination of total water in refractory minerals. Groves (1951) has noted that most rock-forming minerals require temperatures of 800° to 900° C applied over a period of 1 hour or more to release all of their water. He advocates the use of a combustion tube furnace maintained at 1000° C for 1 hour and the absorption of the released water in absorption tubes. Application of the combustion tube method to chromite in this laboratory, however, has not produced significantly higher results than those resulting from the Penfield method.

Reelfs (1956) has maintained that the high temperatures used in the Penfield method are sufficient to force the oxidation of ferrous iron by water. By calculation of the water content of the gangue mineral associated with a chromite which Reelfs analyzed, he estimated that 25 percent of the water had been consumed in the oxidation of FeO during the determination of water by the Penfield method.

FeO (FERROUS IRON)

Because of the geologic significance of the oxidation state of the iron, methods for the more accurate determination of ferrous iron in chromite have been the subject of considerable investigation in this laboratory.

Hillebrand and others (1953, p. 907-922) have provided an excellent review of the difficulties involved in the determination of ferrous iron in various rocks and minerals. The determination of ferrous iron in

chromite is made even more difficult by the limited methods of decomposition which are available.

Fortunately, several acids or acid mixtures are known which will decompose chromite and can be used for the determination of the ferrous iron content. These include phosphoric acid, sulfuric acid, phosphoric plus sulfuric acid, and hydrochloric acid.

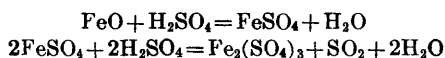
Decompositions using sulfuric acid (Hillebrand and others, 1953, p. 909-912) and hydrochloric acid (Piña de Rubies, 1913; Wichers and others, 1944) require elevated temperatures and pressures and are performed in glass bomb tubes. The chromite sample must in both cases be ground extremely fine. The production of fine powders without the oxidation of a considerable fraction of the ferrous iron is, however, difficult (Hillebrand and others, 1953, p. 907-908; Hartford, 1953).

Caesar and Konopicky (1939) used a phosphoric acid decomposition of chromite to determine ferrous iron. They provided a protective atmosphere of CO_2 during decomposition to prevent the oxidation of ferrous iron. Both the rate of the decomposition of the chromite and the rate of attack on the glass vessel vary directly with the temperature of the solution. This method has given inconsistent results when tried in this laboratory and by others (Seil, 1943).

R. E. Stevens, U. S. Geological Survey (written communication, 1953), studied the use of phosphoric acid in a sealed glass bomb. His results revealed that a considerable blank is present in the procedure. The blank varies with each batch of phosphoric acid used and with each sample. He devised a correction procedure based on a plot of the quantities of permanganate titrant consumed versus the quantity of sample used. This correction procedure still leaves a considerable measure of uncertainty, however.

Smith and Getz (1937) have described the efficiency of a mixture of sulfuric and phosphoric acids as a solvent for chromite. Although this mixture oxidizes Fe(II) it has nevertheless been used as the basis for many of the more recently published procedures for the determination of ferrous iron.

Seil (1943) has explained the oxidation action of this acid mixture as being due to the following 2-step reaction:



Seil used this reaction and the presence of traces of sulfate in phosphoric acid to explain the low and discordant results found when phosphoric acid alone is used for the decomposition of chromite.

This reaction can also be used to explain low results obtained using the Mitscherlich sulfuric acid decomposition of chromite.

According to this reaction, sulfur dioxide is formed in the sealed tube in an amount stoichiometric to the amount of Fe(II) contained in the sample. The success of the Mitscherlich method would then depend upon the recovery of all of the sulfur dioxide liberated. This would require that special precautions be taken when the sealed tube is broken.

Seil (1943) used the sulfur dioxide liberated during the decomposition of chromite with sulfuric plus phosphoric acids as the basis of his method for ferrous iron. The sulfur dioxide is caught in an excess of dichromate solution and oxidized to sulfuric acid. The amount of dichromate reduced is then determined and is equivalent to the original Fe(II) content of the sample.

A modification of this procedure is one of the methods (method 3, see p. 62) used in this laboratory and by at least several industrial laboratories. Seil used an atmosphere of purified carbon dioxide under vacuum as a carrier gas. Most chemists find it more simple to use a commercially purified inert gas under pressure. Ball-joint fittings on the glassware simplify many of the manipulations.

The method has been found to give very precise results. One disadvantage, as far as routine work is concerned, is the time taken for each decomposition. At a temperature low enough to avoid attack of the glass reaction flask, decomposition of some chromite may require 3-4 hours. The number of absorption trains that can be set up is usually limited.

Shein (1937a) has also proposed a method that circumvents the oxidizing action of sulfuric-phosphoric acid mixtures. A known excess of vanadium pentoxide is added to the decomposition mixture to oxidize the Fe(II) in solution. The reduced vanadium formed is much less amenable to air oxidation. The excess vanadium remaining in solution is then titrated to determine the equivalent amount reduced by the Fe(II). The mechanism of the reaction involved in this procedure in the light of Seil's explanation (1943) would involve the reduction of vanadium by the sulfur dioxide formed.

Several variations of Shein's procedure have been described (Balyuk and Mirak'yan, 1949; Samanta and Sen, 1946; Nagaoka and Yamazaki, 1954). A variation of the Shein procedure is in use in the rapid analysis laboratory and is among those described in detail (method 1, p. 61).

Several of the investigators cited have emphasized the necessity for preoxidizing the acid mixture before it is reacted with the chromite. Presumably the nature of the reaction taking place when the acid mixture is heated is such as to reduce the vanadium. If not preoxidized, subsequent titration of this reduced vanadium would yield high results. The results actually obtained by this

method in this laboratory are usually higher than those obtained by the other methods used. This would indicate that the reaction taking place during heating continued to take place during the digestion of the chromite. The nature of this reaction and the means that might be taken to circumvent it are unknown at this point.

Soon after this description of chromite analysis was written a method recently published by Goswami (1957) was noted which seems to overcome the major objection raised against the Shein- V_2O_5 procedure. Goswami reports that in his trials of the Shein method 16-20 percent of the V_2O_5 present in solution was decomposed in addition to the amount required to oxidize the ferrous iron in the sample. To get around the uncertainty and high blank which this causes, he proposes the use of ceric sulfate instead of vanadium pentoxide as the oxidizing agent. The sample is decomposed at 290° to 300° C with a 4+1 mixture of phosphoric and sulfuric acids in the presence of excess ceric sulfate. The excess ceric ion is then determined by titration with standard ferrous sulfate solution and the amount consumed in the oxidation of the ferrous iron calculated. Consistent and reproducible results are claimed.

Goswami's modification has not as yet been tried in this laboratory. It shows promise, however, of overcoming a major objection to what could otherwise be a simple and accurate method for the determination of ferrous iron.

Shein (1937a, b) has also devised an entirely different procedure which is very simple in principle. The two principal steps consist of an ignition in an inert atmosphere and a re-ignition in an atmosphere of oxygen. The weight gained between the two ignitions represents the gain in oxygen of the FeO as it is oxidized to Fe_2O_3 . This method is also used in this laboratory and is among those described in the procedure (method 2, p. 62).

The principal advantage of the ignition method is that it offers an entirely different procedure for the determination of ferrous iron and increases the possibility for accuracy. Since the sample is not consumed during the determination it is also possible to perform a complete analysis on the same sample. This can be important if only small amounts of material are available.

This method is time consuming only in the measure of the elapsed time. It does not require much of the analyst's attention. If special furnaces can be constructed to heat a number of samples simultaneously the elapsed time per sample can be reduced to reasonable proportions.

One of the most common criticisms of the method relates to the unfavorable multiplication factor involved in the conversion of the

weight (O_2) gained to FeO. In actual practice, however, the error introduced by this multiplication is relatively minor.

Assume that a 1-g sample has been taken and that a 10 mg gain in weight has been registered after ignition in oxygen. If the gain in weight can be measured to the nearest 0.02 mg (semimicro balance) this would produce an uncertainty of only 4 parts in 1,000, namely, 10.00 ± 0.02 mg. Multiplication of this weight gain by the conversion factor (9.0) gives a FeO content of 90.00 ± 0.18 mg, still expressed with the same 4 parts per 1,000 uncertainty. This corresponds to an FeO content of 9.000 ± 0.018 and a precision which most analysts would be willing to accept for the determination of ferrous iron. The error produced by rounding off the conversion factor for converting oxygen gain to FeO content (8.981) produces an error of the same order of magnitude.

If the weight uncertainty can be held to only 0.1 mg, this procedure gives an uncertainty of 1 part in 100 in the determination. Most analysts would accept this precision.

In actual practice the major uncertainty associated with this determination is the uncertainty involved in the oxidation of the sample. Some studies of the oxidation of ferrous iron in magnetite (Ralston, 1929) indicate that the oxidation is not complete at $1000^\circ C$. Another study (Hillebrand and others, 1953, p. 524) indicates that Cr_2O_3 always undergoes oxidation to higher oxides during ignition.

For practical purposes it seems best to regard the oxidation empirically and to abide closely by the arbitrary conditions preset for the determination.

Investigations in this laboratory have shown that continued oxidation of some chromite ore, for example, National Bureau of Standards standard sample 103 (chrome refractory) will result in a continuing weight gain as the sample is heated beyond one hour. In some samples continued oxidation results in an indicated ferrous iron content that is greater than the total iron in the sample calculated as FeO.

It has also been found that a finely ground sample (about 100 mesh) will yield a higher apparent FeO content than a coarser sample (about 30 mesh) of the same material. As already noted, however, excessively fine grinding (200 mesh or finer) will cause a significant oxidation during the grinding operation itself. The grinding operation recommended by Hartford (1953) seems to be a reasonable compromise. A 7-g sample is ground in an automatic mortar for half an hour.

The ease of oxidation is also affected by the amount and nature of the gangue materials in the sample. Siliceous gangue surrounding the chromite particles may retard the oxidation significantly.

The composition of the materials used as the ignition boats can also be critical. Porcelain boats fuse to one another during ignition and significant amounts of foreign materials are liable to be recorded as ferrous iron. Platinum boats can be used except that the ignited samples adhere tenaciously to the metal and are difficult to scrape.

Boats made of either fused quartz, alundum, or stabilized zirconia seem to possess all the necessary qualifications. They do not adhere to one another during ignition; they do not fuse and pick up foreign materials; they show no apparent weight change during ignition; and they can be reused time and time again. Silica boats allow the sample to be scraped out completely after ignition. Alundum boats can be easily notched for identification.

It is advisable to use two boats, one slightly larger than the other to allow nesting. The bottom boat serves as a carrier and is not weighed. It protects the weighed boat from foreign materials that may have been spilled in the furnace tube or chamber.

In spite of the difficulties and disadvantages the ignition method has been used by a number of analysts (Balyuk and Mirak'yan, 1949; Samanta and Sen, 1946; de Wet and Van Niekerk, 1952), seemingly successfully. If the oxidation could be performed on a less empirical basis the determination could be performed with a greater measure of confidence. It would be interesting to see the application of the thermobalance to this problem.

METHOD 1: SHEIN- V_2O_5 PROCEDURE

REAGENTS

Acid mixture: Add 3-g V_2O_5 to a solution containing 300 ml H_3PO_4 (conc.) and 600-ml H_2SO_4 (conc.). Heat until the V_2O_5 dissolves. Add 0.5-ml increments of 0.1 N $KMnO_4$ until a small portion of the solution diluted with water indicates a slight excess of $KMnO_4$ to be present. Heat until white fumes are evolved. Cool.

Standard $KMnO_4$ solution: 0.1 N.

Cobaltous sulfate solution: 10 percent.

PROCEDURE

1. Transfer 0.250 g of sample and standard chromite to a 150-ml beaker.
2. Wet the sample with water until it is well dispersed.
3. Add 30 ml of the acid mixture and mix.
4. Heat in an oven at $220^\circ C$ overnight.
5. Allow to cool.
6. Dilute the viscous solution with water and transfer to a 400-ml beaker. Dilute to approximately 200 ml.
7. Add 25 ml of the cobaltous sulfate solution. (This step is omitted if the end point is determined potentiometrically.)
8. Titrate with the standard permanganate solution, to the appearance of an end point (visually or potentiometrically).

CALCULATION

Determine the titration factor by dividing the percent FeO in a standard sample by the volume of permanganate solution consumed.

Multiply each of the titrations by the titration factor.

Determine the blank correction by determining the ferrous iron content of a number of samples in the series by each of the other two methods described below. Subtract the correction blank from each determination to obtain the corrected percent FeO.

METHOD 2: SHEIN-IGNITION PROCEDURE**EQUIPMENT**

Hinged, top-opening tube furnace.

2 quartz combustion tubes.

N₂: Specially purified; "free" of O₂.

O₂: Commercial grade.

PROCEDURE

1. Transfer 0.500 g of sample to an alundum or fused quartz combustion boat
- (1). Spread the sample out evenly.
2. Place boat (1) into a somewhat larger boat made from alundum, or fused quartz.
3. Position both boats in the cool quartz tube.
4. Sweep the air from the tube with N₂ for 10 minutes (1,000 ml per min).
5. Lower the rate of flow of N₂ to approximately 10 ml per min.
6. Insert the tube carefully into the opened furnace (preheated to 900° C).
7. Heat for 30 minutes.
8. Remove the tube from the furnace and cool to almost room temperature, N₂ flow being continued.
9. Remove the combustion boats and allow them to come to room temperature in a desiccator.
10. Weigh boat (1) to the nearest 0.01 mg.
11. Repeat the above operations in an atmosphere of O₂, heating the boats at 1000° to 1100° C for 1 hour.
12. Reweigh boat (1).

CALCULATION

$$\text{Percent FeO} = \frac{\text{weight gain} \times 9 \times 100}{500}$$

METHOD 3: SEIL'S EVOLUTION METHOD**REAGENTS**

Acid mixture: Add 100-ml H₂SO₄ (conc.) to 400-ml H₃PO₄ (conc.). Heat to fumes and fume for 15 minutes.

Standard dichromate solution: 0.1 N.

Sulfuric acid: 1 + 1.

Mohr's salt solution: Same as that used for Cr₂O₃ determination.

N₂: "Free" of O₂.

Indicator solution: Same as that used for the Cr₂O₃ determination.

EQUIPMENT

Reaction flask: For occasional use, a commercially available 200-ml round-bottom flask with side arm and spherical ball joint can be used. For continuous use a specially made flask with heavy walls and bottom is preferred. This flask with adaptor is shown in figure 8.

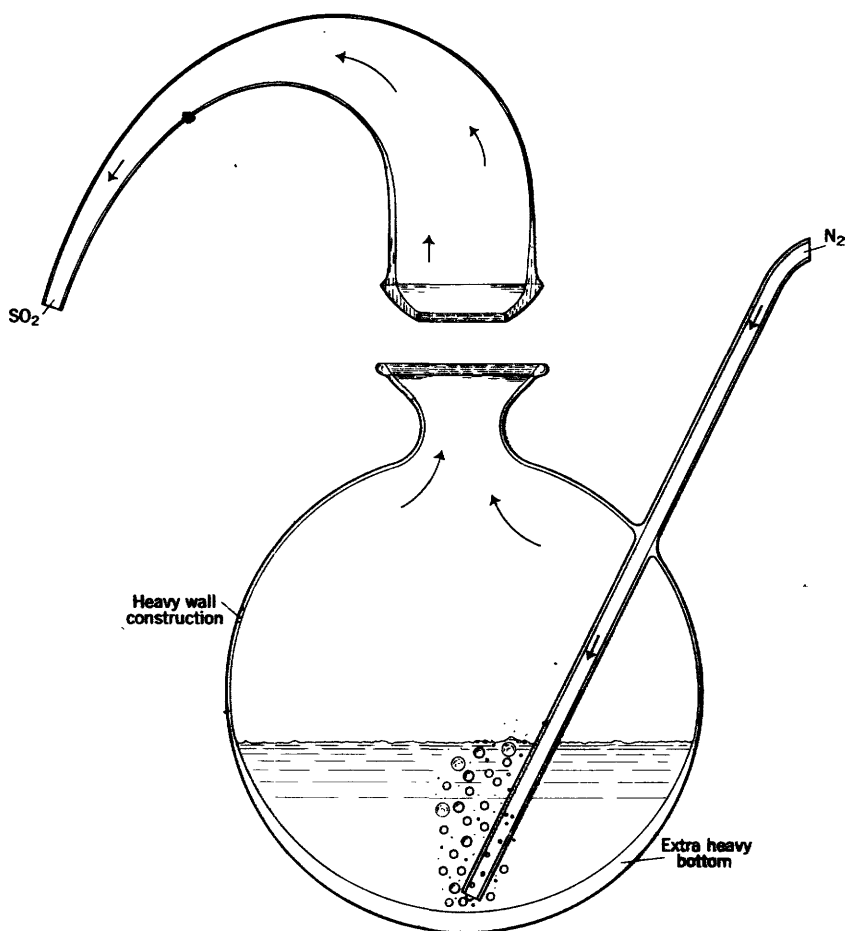


FIGURE 8.—Reaction flask for the determination of ferrous iron by Seil's method.

PROCEDURE

1. Transfer 0.500 g of sample to a specially constructed reaction flask (fig. 8).
2. Wet slightly with water to disperse the sample.
3. Add 25 ml of the acid mixture.
4. Insert the flask into an absorption train consisting of two absorption bottles containing a known amount of standard dichromate solution (25 ml) and water (150 ml).
5. Start flow of N_2 through the train.
6. Heat the flask gently at a controlled temperature to no more than 220°C . Maintain this temperature until the sample is completely dissolved.
7. Cool the flask.
8. Disconnect the train and gather the two solutions plus washings together into a 600-ml beaker.
9. Add 25 ml of indicator solution.
10. Add an excess of the Mohr's salt solution and back titrate to the end point with the standard dichromate solution.

CALCULATION

1-ml 0.1 N $K_2Cr_2O_7 = 0.00717\text{-g FeO}$

Milliliter of $K_2Cr_2O_7$ solution in absorption tubes plus milliliter of $K_2Cr_2O_7$ titration— $K_2Cr_2O_7$ equivalent of the Mohr's salt solution* added= $K_2Cr_2O_7$ equivalent of the FeO in sample.

$$\text{Percent FeO} = \frac{\text{ml of } K_2Cr_2O_7 \times 7.17 \times 100}{500}$$

EXPERIMENTAL RESULTS

The methods described here have been tested by analyzing samples of chrome ore previously analyzed by conventional methods by other laboratories.

Table 2 lists the results obtained at widely different times in the analysis of an industrial chrome-ore standard (Hartford, 1953).

TABLE 2. *Results of analyses of metallurgical chrome-ore standard by rapid methods*

	1	2	3	4	5	6	Certifi- cate analysis ¹
Cr_2O_3	50.9	51.0	50.9	51.0			50.96
SiO_2	4.50	4.47	4.48	4.56	4.47		4.46
Total iron as Fe.....	10.6	10.5	10.6	10.6	10.6	10.5	10.49
Al_2O_3	11.1	11.2	11.0	11.2	11.3	11.1	10.94
TiO_222	.19					² 12
MgO.....	16.8	16.8	16.8	16.9	16.9		16.78
CaO.....							² 40
MnO.....	.12						² 14
V_2O_508						² 07
NiO.....	.50						² 48
Total H_2O	2.0						

¹ Hartford 1953.

² Average of only a few determinations.

Table 3 lists the results obtained in the analysis of fourteen chrome ores previously analyzed by three commercial or industrial laboratories using current variations of conventional methods.

Comparison of the results is not strictly justifiable since the results of three or more analysts are being compared against the results of only one analyst. Because of the nature of the methods, however, and the fact that they depend upon a continuing comparison of results against standard samples, it is felt that the precision is representative of the precision to be expected in a number of analyses by a greater number of analysts.

The rapid methods have to date been applied to more than 100 samples of chromite and chrome ore from Cuba, Philippine Islands, Rhodesia, Turkey, Alaska, Vermont, Maryland, Pennsylvania, Montana, and Transvaal.

TABLE 3.—Comparative analyses of 14 samples of chrome ore

(a: Analyses performed by several analysts in several laboratories using conventional methods (W. H. Hartford, written communication, 1966). b: Analysis performed by author using the rapid methods described in this report]

	1		2		3		4		5		6		7	
	a	b	a	b	a	b	a	b	a	b	a	b	a	b
Cr ₂ O ₃	52.39 52.37	52.4	48.20 48.45	48.2	43.91 44.05 44.15	44.0	51.78 52.09	51.8	53.08	53.7	46.42 46.33 46.77	46.4	46.37 46.77 46.96	46.7
SiO ₂	4.35	4.67	5.06	5.41	3.29 3.10	3.72	4.43	4.77	4.06	4.39	1.43	1.70	.97	1.02
Total iron as FeO.....	12.43 12.99	13.3	10.62 10.61	10.9	19.26	19.4	12.69 12.93	13.1	12.46	12.9	19.21 19.22	19.3	20.09 20.33 20.18	20.3
Al ₂ O ₃ (+TiO ₂).....	12.1	(10.6)	11.45	(10.6)	16.96	(15.7)	11.78	(10.1)	9.94	(10.2)	15.92	(15.4)	13.06	(15.7)
Al ₂ O ₃	10.2	10.3	10.3	10.3	15.0	15.0	14.0	14.2	13.9	13.8	9.99	10.0	10.38	9.6
TiO ₂	13.0	13.5	18.03	18.0	10.08	10.1	14.0	14.2	13.9	13.8	9.99	10.0	10.38	9.6
MgO.....	.25	.20	.26	.19	.23	.23	.25	.21	.25	.17	.17	.29	.21	.21
MnO.....	.10	.10	.09	.09	.30	.24	.16	.16	.12	.12	.26	.25	.21	.21
V ₂ O ₅	1.13	1.13	2.73	2.73		.60		1.26		1.20				
Total H ₂ O.....														
Cr ₂ O ₃	54.4 54.86	54.3	55.44 55.36 55.50	55.4	44.27 44.25 44.32	44.3	53.53 53.51 53.62	53.5	46.84 46.80 46.99	46.7	46.39 46.60 46.59	46.4	53.83 53.92 54.09	53.8
SiO ₂	1.84	1.90	1.55	1.83	3.12	3.35	2.63	2.79	.72 .75	.97	1.18 1.27	1.70	2.38	2.49
Total iron as FeO.....	15.36	15.4	13.88 13.62 13.48	13.6	19.19	19.3	15.31 15.41	15.7	20.26 20.31	20.4	19.30	19.8	15.44 15.48	15.6
Al ₂ O ₃ (+TiO ₂).....	14.65	(13.4)	15.85	(15.4)	15.85	(15.4)	13.90	(13.0)	15.55	(15.1)	15.91	(16.2)	13.65	(12.9)
Al ₂ O ₃		13.0	14.7	14.7				12.6	14.88	14.3		15.5		12.4
TiO ₂41	.67	.67				.43		.75		.68		.47
MgO.....	7.82	8.4	10.82	10.7	10.32	10.7	8.82	8.5	10.07	10.0	10.17	9.7	9.25	8.8
MnO.....	.26	.24	.22	.22	.22	.22	.25	.29	.28	.28	.20	.16	.25	.26
V ₂ O ₅10	.10	.19	.19	.19	.19	.10	.10	.28	.28	.16	.16	.20	.06
Total H ₂ O.....		.40					.47			.04		.29		

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