UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

CHEMICAL METHODS FOR ANALYSIS OF ROCKS AND MINERALS

By

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U.S. Geological Survey
Open-file Report 84-565
1984

This report is preliminary and has not been edited or reviewed
for conformity with Geological Survey standards and nomenclature.

Chemical literature contains an abundance of analytical procedures suitable for rock and mineral analysis. Each of the authors of this manual has trained other chemical analysts in the laboratory. They realized the need for a concise written guide for the trainee. "Chemical Methods for Analysis of Rocks and Minerals" was thus conceived and assembled, intended as a working guide for the chemical analyst. The methods described were derived from many sources and may include minor modifications or adaptations for specific situations or available equipment. The user is referred to published works for the underlying chemical theory. The writers are indebted to C. Tilbury, D. Vivit, and D. Shepard for their advice and assistance in the completion of this guide.

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CLEANING LABORATORY GLASSWARE

It is important that all glassware be scrupulously clean and the inside walls be entirely free of grease. No exact measurements of volume can be made if the walls of the glassware are greasy even to the slightest extent.

1. Rinse glassware with water several times to remove the contained solution.

2. Scrub with a soap solution if particles are clinging to the glassware.

3. Immerse in a H_2SO_4-CrO_3 acid mixture (20.4 g CrO_3/1000 ml H_2SO_4; well leached).

4. Rinse glassware extensively with H_2O at least 7 times and run plenty of H_2O to avoid the subsequent formation of toxic CrO_2Cl_2.

5. Immerse glassware in a HCl-H_2O_2 acid rinse (dilute HCl with a few ml H_2O_2).

6. Rinse with H_2O again several times.

7. Finally rinse several times with distilled-deionized H_2O.

8. Air dry over Whatman No. 1 filter paper.

9. For glassware to be used in determining chlorine, HNO_3 can be exchanged for HCl in the rinse solution.

Compiled by P. Klock

CHOICE AND CARE OF PLASTIC CONTAINERS FOR STORAGE OF TRACE ELEMENT SAMPLES

(From Selection and cleaning of plastic containers for storage of trace element samples by John R. Moody and Richard M. Lindstrom, Anal. Chem., v. 49, no. 14, Dec. 1977, p. 2264-2267)

Twelve different plastics were examined by gravimetry, isotope dilution mass spectrometry, and neutron activation analysis. Teflon and conventional polyethylene (CPE) bottles were the least contaminating once they were cleaned. The study included LPE, PP, PMP, PC, PVC, CPE, TFE, and FEP bottles. Specimens of Tefzel or ETFE, Teflon PFA, PS, and TPT were also examined. The following steps are recommended for cleaning plastic containers:

1. Fill with 1+1 HCl (AR grade).

2. Allow to stand one week at room temperature (80°C for teflon).

3. Empty and rinse, with distilled H_2O.

4. Fill with 1+1 HNO_3 (AR grade).

5. Allow to stand one week at room temperature (80°C for teflon).

6. Empty and rinse with distilled H_2O.

7. Fill with purest available distilled water.

8. Allow to stand several weeks or until needed, changing water periodically to insure continued cleaning.

9. Rinse with purest water and allow to dry in a particle and fume-free environment.

Compiled by M. Cremer

CARE AND USE OF PLATINUM WARE (condensed from "Notes on the Care and Use of Pt Laboratory Ware"[1])

Platinum is a relatively soft metal and regular cleaning, burnishing, and reshaping of the object will prolong the life of the ware. Accurate results from its use are obtained. For a more detailed account of the subject, see ref. 1, 2, and 3.

Platinum Care:

1. After any type of fusion in platinum, soak in 1 + 1 HCl on a steam bath.

2. Rinse thoroughly with distilled H_2O and rub gently with rounded grains of moistened sand which was previously selected and carefully cleaned for use on platinum.

3. Place platinum in the proper reshaping block; burnish or stroke with the platinum grain using a burnishing tool periodically cleaned with a soft crocus cloth.

4. Finish by immersing the platinum in chromic acid cleaning solution (H_2SO_4-CrO_3); rinse thoroughly with distilled H_2O.

5. Finally, ignite the ware at 1000°C for 1/2 hour; store in a desiccator to cool. Inspect the platinum for any discoloration. If the platinum is bright and shiny, it is ready for reuse. If not, continue with step 6.

6. In the discolored platinum vessel, melt potassium pyrosulfate over a low flame from a Tirrill burner. The white SO_3 fumes, the cleansing agent, should escape only slowly. Place vessel on a porcelain plate to cool. Gently knock out the hardened melt; place the platinum in boiling H_2O until the balance of the melt dissolves.

7. Again clean the platinum in chrome-sulfuric acid, rinse and reignite, cool, and again check for discoloration. Steps 6 and 7 must be repeated until the platinum is no longer dark.

If platinum was used only to drive off surface moisture in samples (105 ± 5°C), a thorough brushing and cleaning in 1 + 1 HCl will suffice. Drying the clean platinum at 105° is adequate in this case. At elevated temperatures, platinum slowly volatizes.

Platinum Use:

Platinum is attacked under the following conditions:

By heating in the following liquids:

1. Aqua Regia.

2. Hydrochloric acid and oxidizing agents.

3. Concentrated sulfuric acid. The action is extremely slow and, for all laboratory purposes, negligible.

4. Concentrated phosphoric acid. Here again the action is noticeable only after very prolonged heating.

By heating in the following solids, their fusions or vapors:

1. Sulfur, selenium, and tellurium. The action of sulfur vapor is very slow, and prolonged heating is required to produce any serious effect; selenium and tellurium readily combine with platinum.

2. Phosphorus, arsenic, and antimony. Combination with platinum occurs readily.

3. Magnesium pyrophosphate above 900^{o}C.

4. Silica and borax at high temperatures.

5. Molten lead, zinc, tin, bismuth, silver, gold, or copper or mixtures which form these metals by reduction.

6. Fused alkali oxides and peroxides, and, to a smaller extent in the presence of air, alkali hydroxides.

7. Fused nitrates. The action is intensified by the presence of alkali hydroxides or carbonates, but in no case is it very severe.

8. Phosphorus pentoxide or phosphoric acid. The action is relatively little.

9. Fused cyanides. Platinocyanides are formed.

10. Iron oxide above 1200^{o}C. Oxygen is liberated and the iron combines with the platinum.

11. Silica, silicates, alumina, and magnesia above 1600^{o}C. At lower temperatures, no action occurs.

12. Fused alkali and alkali chlorides in the presence of air at 1000^{o}C or above.

13. Lead and bismuth oxides above 1250^{o}C.

Compiled by P. Klock

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1. J. Bishop & Company, Notes on the care and use of platinum laboratory ware.

2. Kolthoff, I. M., and Sandell, E. B., 1952, Textbook of quantitative inorganic analysis, 3rd ed.: New York, Macmillan Company, 759 p.

3. Kolthoff, I. M., Sandell, E. B., Meehan, E. J., and Bruckenstein, Stanley, 1969, Quantitative Chemical Analysis, 4th ed., London, Macmillan Company, Collier-Macmillan.

SAMPLE HANDLING-MIXING

All the careful work put into a good analysis (gravimetric or instrumental) will be for naught if the sample taken is not representative of the original material. Laboratory samples of rocks and minerals require frequent mixing, to minimize segregation of minerals by gravity due to everyday packing, usage, and handling.

Before any analysis, and every two weeks thereafter during analysis, each sample is mixed using a technique termed "coning and quartering"[1].

Procedure

1. Completely empty sample bottle on an 8" x 12" sheet of Albanene paper (100 percent rag).
2. Roll powder over itself 100 times, by raising the corners of the paper in succession.
3. Using a spatula, split the sample into quarters.
4. Carefully transfer one set of opposite sides back into original container (do not pack).
5. Combine the other set of opposite sides and repeat steps 2-5.
6. Repeat the procedure until sample container is full (discard excess sample).

Compiled by P. Klock

REFERENCE

1. Kolthoff, I. M., and Sandell, E. B., 1952, Textbook of quantitative inorganic analysis, 3rd ed.: New York, Macmillan Company, 759 p.

COLORIMETRIC Al_2O_3

(Adapted from The Direct Microdetermination of Silicon and Aluminum in Silicate Minerals; U.S. Geological Survey Professional Paper 650-B, p. B136-B139, Robert Meyrowitz).

Alumina (Al_2O_3) is determined spectrophotometrically by measuring the absorption of light at 475 nm by a calcium aluminum Alizarin Red-S complex. The sample is fused with $LiBO_2$, dissolved in 4 percent HNO_3, and made to volume. The colored complex is developed by taking an appropriate aliquot to which is added $CaCl_2$, $NH_2OH.HCl$, $K_3Fe(CN)_6$, mercaptoacetic acid (a.k.a. thioglycolic acid), buffer, and Alizarin Red-S. The usual concentration of fluorine found does not interfere, but appreciable quantities of iron and titanium also form colored complexes that absorb at 475 nm. Iron can be tolerated in a ratio to Al_2O_3 of two to one. Titanium interference is not eliminated but is corrected from an empirically derived table.

Reagents (all chemicals-reagent grade):

Calcium chloride solution: Transfer 7 g of $CaCO_3$ to a 250 ml beaker. Add 50 ml of H_2O and then add dilute HCl dropwise with constant stirring until all $CaCO_3$ is dissolved. Boil the solution for 1 or 2 minutes to remove the dissolved CO_2. Cool. Filter through a fast paper; dilute to 500 ml and mix well.

Hydroxylamine hydrochloride solution, 10 percent (w/v): Prepare and filter.

Potassium ferricyanide solution, 0.75 percent: Prepare fresh each day.

Mercaptoacetic acid solution (a.k.a. thioglycolic acid), 1.6 percent (v/v): Prepare fresh each day.

Buffer solution: Prepare 500 ml solution to contain 100 g sodium acetate, $NaC_2H_3O_2.3H_2O$. Filter through a fast filter paper.

Alizarin Red-S (alizarin sodium monosulfonate) solution, 0.05 percent (w/v): Prepare 500 ml; filter through a slow paper.

Procedure	Comments
1. Thoroughly mix and quarter samples, NBS 99a or equivalent, and one or two other standard rock powders whose Al_2O_3 value does not exceed 19 percent.	1. The 19 percent limitation insures a final Al_2O_3 concentration not to exceed 0.95 ppm, the upper limit for this procedure. If SiO_2 was determined, steps 1-5 are omitted. An aliquot of the solution developed for SiO_2 is used in step 6.

2. Into a glazed black porcelain crucible weigh 40 mg of sample. Add to the crucible 350 mg $LiBO_2$. Mix thoroughly with a platinum rod or stainless steel spatula, and transfer the mixture to a graphite crucible as described in Na and K procedure.

3. In the same manner, prepare 40 mg, 30 mg, and 20 mg mixtures of NBS 99a to be used as a calibration curve. Also prepare 40 mg mixtures of the other standard rock powders to be used to test the procedure.

4. Prepare a blank by weighing 350 mg of $LiBO_2$ and transferring it to a graphite crucible.

5. Proceed with Steps 4 through 6 of "Procedure for Colorimetric Determination of SiO_2".

6. To develop the complex, transfer 3 ml aliquots of each solution to a series of 100 ml volumetric flasks.

2. No more than 41.5 mg of NBS 99a should be weighed or the 0.95 ppm limit will be exceeded. NBS 99a is a soda feldspar with insignificant amounts of titanium and iron.

6. Three milliliters of the original solution results in no solution greater than ~0.91 ppm in Al_2O_3 or

$$\frac{\left(\frac{40\ \text{mg}}{250\ \text{ml}}\right)\left(1000\ \frac{\mu\text{g}}{\text{mg}}\right)(0.1906)\ (3\ \text{ml})}{100\ \text{mg}} \approx 0.91\ \frac{\mu\text{g}}{\text{ml}}$$

because $[Al_2O_3]$ in NBS 99a = 19.06 percent.

7. To each solution, add 2.0 ml $CaCl_2$ solution, 1.0 ml hydroxylamine hydrochloride, 1.0 ml potassium ferricyanide, and 2.0 ml of mercaptoacetic acid. Allow to stand for 5 minutes.

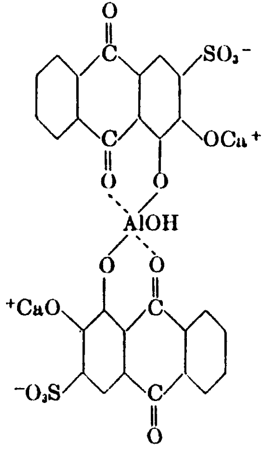
8. Add 10.0 ml buffer solution. Allow to stand for 10 minutes.

9. Add 10.0 ml of Alizarin Red-S solution with a volumetric pipet. Dilute to mark, mix, and let stand for 45 to 75 minutes. Measure absorbance at 475 nm.

10. Treat the NBS standard feldspar data by the least squares method.

7. An easier and permissible method is to mix together sufficient portions of 2.0 ml $CaCl_2$ solution, 1.0 ml hydroxylamine hydrochloride, and 1.0 ml potassium ferricyanide. Then add to each solution 4 ml of the mixture and 2.0 ml mercaptoacetic acid. Potassium ferricyanide and mercaptoacetic acid serve as complexing agents for iron. Some sample solutions turn green with the addition of $K_3Fe(CN)_6$; some solutions become colorless with the addition of mercaptoacetic acid; any color remaining in any sample solution vanishes with the addition of the buffer.

9. The complex is formulated as follows:



11. Calculate the apparent Al_2O_3 content of the unknowns and the rock standards. Check the accuracy of [Al_2O_3] in the rock standards against the "true" values by correcting the apparent [Al_2O_3], calculated from the equation, for TiO_2 interference. Use the table given below. Correct the [Al_2O_3] in the unknowns in the same manner.

Apparent Percent Al_2O_3	Correction Percent TiO_2
0	0.25
5	0.20
10	0.15
15	0.10
20	0.05

(Apparent percent Al_2O_3) minus [(Correction per percent TiO_2) (percent TiO_2)]=Percent Al_2O_3.

11. The percent TiO_2 is known in the rock standards. However, before the correction to the unknowns can be made, percent TiO_2 is determined as set forth in the procedure for colorimetric TiO_2.

Compiled by M. Cremer

CHLORINE

(Adapted from New Colorimetric Determination of Chloride using Mercuric Thiocyanate and Ferric Ion, by Iwasaki, I., Utsumi, S., and Ozawa, T., Bulletin of the Chemical Society of Japan, v. 25, p. 226, 1952)

An aliquot of the solution from the leached sinter prepared for the fluoride determination (digestion method) is used to develop the orange color of ferric thiocyanate. Ferric nitrate and mercuric thiocyanate are added; the solution is made to volume, and absorbance is read at 465 nm. The method is rapid and simple for low concentrations of chloride.

Reagents (all chemicals-reagent grade):

Ferric Nitrate. Dissolve 70 grams of $Fe(NO_3)\cdot 9\ H_2O$ in water containing 30 ml of concentrated nitric acid and dilute to one liter with water. Filter through Whatman no. 42 paper.

Mercuric thiocyanate. Dissolve 0.3 g of mercuric thiocyanate in 100 cc absolute ethyl alcohol.

Sodium Chloride Standard. Dissolve in H_2O 1.648 g dry NaCl (2 hours at 105° C). Make to one liter volume.

Procedure	Comments
1. To a 10 ml rock or mineral solution in a 50 ml volumetric flask, add 5.0 ml of ferric nitrate solution.	1. The reactions are as follows: $2\ Cl^- + Hg(CNS)_2 \rightleftharpoons HgCl_2 + 2\ CNS^-$ $4\ Cl^- + Hg(CNS)_2 \rightleftharpoons HgCl_4^{--} + 2\ CNS^-$ $CNS^- + Fe^{+++} \rightleftharpoons Fe(CNS)^{++}$
2. Add 1 ml of mercuric thiocyanate in absolute alcohol. Dilute to mark and mix.	
3. At the same time, prepare a series of NaCl standards in the same manner.	3. The minimum determinable concentration is 0.05 ppm. However, best results are obtained in the range 0.1 - 20 ppm Cl^-.

4. After 10 minutes, measure absorbance at 465 nm. Prepare a calibration curve by the method of least squares. Report percent Cl^- in the unknowns to only one decimal place.

4. The color is stable for several hours. Bromide, iodide, cyanide, thiosulfate and nitrate interfere. The curve is not exactly linear. The determination is regarded as somewhat qualitative.

Compiled by M. Cremer

COLORIMETRIC DETERMINATION OF TOTAL IRON

Total iron as Fe_2O_3 is determined by forming an orange-colored Fe(II)-orthophenanthroline complex in weakly acid, neutral or weakly alkaline solutions (pH2-9). Beer's law is closely followed. The color is stable for many months. The iron in the sample is reduced with hydroxylamine hydrochloride. Orthophenanthroline is added, and the solution is buffered with sodium citrate. Given the same original solution described below, the recommended aliquot will accommodate as much as 15 percent Fe_2O_3.

Reagents (all chemicals-reagent grade):

Hydroxylamine hydrochloride (10 percent): dissolve 50 g $NH_2OH.HCl$ in water and dilute to 500 ml. Filter.

Orthophenanthroline solution (0.1 percent): dissolve 0.5 g o-phenanthroline monohydrate in water and dilute to 500 ml. Filter. Keep solution out of sunlight. Discard if color develops.

Sodium citrate solution (10 percent): dissolve 50 g $Na_3C_6H_5O_7.2H_2O$ in water and dilute to 500 ml. Filter.

Standard iron solution: Dissolve 1.000 g of iron metal strip or wire (99.9 percent pure) in 20 ml of 1:1 HCl and dilute to one liter to provide 1000 μg/ml Fe.

Procedure	Comments
1. To a series of 50 ml volumetric flasks, add 15 ml each of solutions containing blank, rock standards, and samples.	1. The sample solutions to be used are those prepared for the colorimetric determination of SiO_2; i.e. 40 mg sample, 350 mg $LiBO_2$ → 250 ml of 4 percent HNO_3. However, the procedure may also be used on fusions of 100 mg samples diluted to 100 ml (see Na and K procedure). In that event, a smaller aliquot is used; i.e. 10 ml → 50 ml.
2. Prepare a series of standard iron solutions using the 1000 ppm iron standard for atomic absorption. To each, add HNO_3 and $LiBO_2$ to match the sample solutions.	
3. To each, add 5 ml of hydroxylamine hydrochloride. Swirl to mix and allow to stand for one hour.	3. An hour wait is recommended by C. O. Ingamells who states that iron must be completely reduced before citrate is added.
4. Pipet 10 ml of 0.1 percent o-phenanthroline solution to each flask and swirl to mix.	4. This reagent forms a reddish-orange complex, $(C_{12}H_8N_2)_3$ Fe^{++}, with Fe(II) in acidic, neutral or basic solution (pH2-9). Beer's law is followed closely.

5. Pipet 10 ml of 10 percent sodium citrate to each flask and swirl to mix.	5. Buffer.
6. Dilute to volume, mix thoroughly, and allow to stand for one hour, or overnight if more convenient.	6. Since the complex is extremely stable, the solutions show no change in color even after many months.
7. Measure the absorbance of the complex at 510 nm using H_2O to set zero absorbance.	
8. Prepare a linear equation by least squares using the data from the standard solutions. Compute percent Fe_2O_3 in the rock standards and the unknowns. Check percent Fe_2O_3 in the rock standards against the "true" values.	

Compiled by M. Cremer

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Bandemer, S. L., and Schaible, P. J., 1944, Determination of iron: Ind. and Eng. Chemistry, Anal. ed., v. 16, p. 317-319.

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Sandell, E. B., 1959, Colorimetric Determination of Traces of Metals: 3rd ed., New York Interscience Publishers, Inc., p. 537-542.

Shapiro, Leonard, Rapid Analysis of Silicate, Carbonate, and Phosphate Rocks—Revised edition: U.S. Geol. Survey Bull. 1401, p. 47-48.

COLORIMETRIC DETERMINATION OF PHOSPHORUS

(Adapted from Colorimetric Determination of Phosphorus as Molydivanadophosphoric Acid, R. E. Kitson and M. G. Mellon, Industrial and Engineering Chemistry, v. 16, no. 6, 1944.)

Samples are fused with lithium metaborate and dissolved in nitric acid. The phosphate is brought into solution as orthophosphate. Ammonium vanadate is added to the acidic orthophosphate solution. An excess of ammonium molybdate is added, and the yellow heteropoly complex, molydivanadophosphoric acid, is formed. Spectrophotometric measurement is made at 460 nm. Beer's law is reported to apply up to 40 ppm phosphorus.

Reagents (all chemicals-reagent grade):

Phosphate Standard: 4.3937 gram twice recrystallized potassium dihydrogenphosphate made to one liter in water. 1 ml = 1000 μg P.

Ammonium molybdate: 5 percent solution of the salt $(NH_4)_7Mo_7O_{24}\cdot 4H_2O$ dissolved in warm water (50°C). Filter.

Ammonium vanadate: 0.25 percent solution prepared by dissolving 2.5 grams of NH_4VO_3 in 500 ml of boiling water, cooling the solution somewhat, adding 20 ml of concentrated nitric acid and diluting to one liter after allowing the mixture to cool to room temperature.

Procedure	Comments
1. Mix 100 mg of sample with 700 mg $LiBO_2$ and transfer to a graphite crucible. Prepare a series of rock standards and a reagent blank at the same time in the same manner.	1. If a total analysis has been requested, the fusion made for K and Na may be used, provided that the anticipated percent P_2O_5 is high enough so that only an aliquot of the total solution is sufficient.
2. Fuse the samples and standards for 15 minutes at 950° C. Pour each molten bead into ~ 50 ml of H_2O which contains 7.3 ml HNO_3. Stir magnetically for 15 minutes.	2. The color complex will ultimately be developed from the whole sample. Therefore, 7.3 ml of HNO_3 is needed to control the acidity.
3. Add in order, with adequate mixing, 10 ml of 0.25 percent ammonium vanadate solution and 10 ml of 5 percent ammonium molybdate solution. Transfer to 100 ml volumetric flasks, dilute to mark with H_2O and mix well.	3. Reagents should be added in the order mentioned. If molybdate is added before vanadate, yellow molybdiphosphoric acid is formed with the danger of a colloidal dispersion of ammonium molybdiphosphate which does not disappear on adding vanadate. The whole sample is taken to provide 0.1 to 5 mg of phosphorus for 1-cm cells.

4. Prepare a series of standards as follows:

    Dissolve 3.5 g $LiBO_2$ in H_2O which contains 36.5 ml HNO_3. Make to 250 ml volume with H_2O. With a graduate, add 50 ml to each of four 100-ml flasks to which 250, 500, 1000, and 2000 µg has been added respectively. Prepare the complex as in step 3 above.

5. Allow the solutions to stand overnight so that the inevitable graphite particles settle to the bottom of the flasks. Measure the absorbance at 460 nm.

6. Prepare a calibration curve by the method of least squares. Compute percent P_2O_5 in the rock standards and the unknowns.

4. A 2.5, 5, 10, and 20 ppm standard, with approximately the same pH as the samples, should result.

5. Solutions containing $\geq$ 5 ppm are stable at least 7 weeks. Below this concentration, color increases slowly amounting to 2 percent transmittance in approximately 2 weeks.

6. Rock standards are carried through the procedure as controls.

Compiled by M. Cremer

COLORIMETRIC DETERMINATION OF SILICA

(Adapted from the Direct microdetermination of silicon and aluminum in silicate minerals,
R. Meyrowitz, U.S. Geol. Survey Prof. Paper 650-B, 1969, p. B136-B139.)

In many cases, complete analyses are requested on very small rock and mineral samples. The following procedure has been successfully utilized in the analysis of silicates and phosphates. Constituents which may be determined instrumentally in the resulting solution include SiO_2, Al_2O_3, Total Fe as Fe_2O_3, TiO_2, P_2O_5, CaO, MnO and MgO. In the silica determination, an appropriate aliquot is reacted with ammonium molybdate to form a yellow silico-12-molybdate complex, which is then buffered with tartaric acid before reduction to heteropoly molybdenum blue. Color intensity is then compared spectrophotometrically to similarly treated rock standard solutions and percent SiO_2 is calculated.

Reagents (all chemicals-reagent grade):

$LiBO_2$, anhydrous powder.

HNO_3, concentrated.

Ammonium molybdate solution: Dissolve 3.75 g of $(NH_4)_6Mo_7O_{24}.4H_2O$ in 35 ml H_2O in a 50 ml Tri-Pour beaker containing a Kel-F-covered magnetic stirring bar. Add 5.0 ml 18N H_2SO_4. Stir until dissolved. Cool. Filter through a Whatman No. 40 paper into a 50-ml volumetric flask. Dilute to mark.

Tartaric acid, 10 percent: Weigh 20 g tartaric acid. Dissolve in H_2O in a 200-ml volumetric flask. Filter for storage. Prepare fresh when sediment appears.

Reducing solution: Dissolve 9.0 g sodium bisulfite ($NaHSO_3$) in 80 ml H_2O in a 100 ml Tri-Pour beaker containing a Kel-F covered magnetic stirring bar. In another 100-ml Tri-Pour beaker containing 10 ml H_2O and magnetic stirring bar, dissolve 0.7 g sodium sulfite (Na_2SO_3). Add 0.15 g of 1-amino-2-naphthol-4-sulfonic acid to the sulfite solution and stir until completely dissolved. Add the 80 ml bisulfite solution to the combined solution and mix thoroughly. Filter through a Whatman No. 40 paper into a 100-ml volumetric flask. Dilute to volume with water and transfer to a plastic bottle for storage. Prepare fresh daily.

Procedure	Comments
1. Into a black-glazed porcelain crucible, weigh 40 mg rock or mineral powder.	1. This method has been used successfully on samples ranging in weight from 25 to 50 mg. If more than the analysis of SiO_2 is requested, check the appropriate procedure so that the necessary rock standards will be fused at the same time.
2. Add to the crucible 350 mg $LiBO_2$. Thoroughly mix the powders together with a platinum rod or stainless steel spatula. At the same time, weigh a 350-mg portion of $LiBO_2$, for use as a blank, and carry it, with the samples, through the whole procedure.	2. A series of rock standard materials whose composition approximates that of the unknowns should be treated in the same manner so that a calibration curve may be prepared from their "true" values.

3. Carefully transfer the powder-flux mixture to a graphite crucible of the type described in the determination of Na and K.	
4. Heat for 15 minutes in a muffle furnace at 950^0 C.	
5. Remove the crucible from the muffle and swirl it briefly to cause the molten material to coalesce. Pour the melt into a 250-ml Tri-Pour beaker containing a Kel-F covered magnetic stirring bar, 200 ml water, and 10 ml concentrated HNO_3. Cover and mix on a magnetic stirrer for at least 5 minutes or until dissolved.	5. If the concentration of SiO_2 in solution exceeds that of approximately 200 µg/ml, polymers form. Reaction with ammonium molybdate does not occur. A 50-mg sample containing as much as 68.66 percent SiO_2 (NBS 99a, soda feldspar) at a 200 and 250 ml dilution contains only ~172 and 175 µg/ml SiO_2 respectively.
6. Quantitatively transfer the solution to a 250-ml volumetric flask, carefully rinsing the beaker and making the solution to volume with water.	
7. For determination of SiO_2, transfer 5-ml aliquots of both standards and unknowns to 100-ml volumetric flasks. Add approximately 50 ml water and mix by swirling.	
8. Add 2.0 ml ammonium molybdate solution, swirl, and let stand 10 minutes.	8. The silica (present as silicic acid) reacts with molybdate to form a yellow silico-12-molybdate complex.
9. Add 4.0 ml 10 percent tartaric acid and swirl.	9. Tartaric acid acts as a buffer to adjust the pH in preparation for the next step.
10. Add 1.0 ml of the $Na_2SO_3/NaHSO_3$/1-amino-2-naphthol-4-sulfonic acid reducing solution. Dilute to the mark and mix thoroughly.	10. The reducing solution reacts with the yellow silico-12-molybdate complex and reduces it to heteropoly molybdenum blue.
11. Let stand a minimum of 30 minutes, then measure the absorbance at 650 nm, using water to set the spectrophotometer to zero.	11. Color complex is stable for several days.
12. Weight correct the percent concentrations of the rock standards. Use the corrected concentrations plus the absorbance values to obtain a slope-intercept linear equation. From this equation, calculate the concentrations of the samples. Weight correct the concentrations back to the original sample weight.	

Compiled by S. Neil,

COLORIMETRIC TiO_2

(Adapted from Rapid Analysis of Silicate, Carbonate, and Phosphate Rocks - Revised Edition
by Leonard Shapiro, Geological Survey Bulletin 1401)

When Tiron (disodium-1,2-dihydroxylbenzene-3,5-disulfonate) is added to titania (TiO_2), a yellow color is produced. Ferric iron, an interferer, also reacts with Tiron to form a purple solution which must be decolorized by reduction with sodium dithionite. An aliquot of a $LiBO_2$ fusion dissolved in 4 percent HNO_3 is used to develop the complex.

Reagents (all chemicals-reagent grade):

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

Buffer solution: Dissolve 80 g of ammonium acetate $NH_4C_2H_3O_2$ and 30 ml of glacial acetic acid in 2 liters distilled water. Filter.

Sodium dithionite, $Na_2S_2O_4$ (a.k.a. sodium hydrosulfite): Dry powder.

Procedure	Comments
1. Transfer 15 ml portions of blank, rock standards, and samples to a series of 150 ml beakers.	1. Solutions used are those prepared for the colorimetric determination of SiO_2, or those prepared for K and Na, when a more appropriate aliquot is used.
2. Use a measuring scoop to add approximately 125 mg of Tiron powder to each beaker.	2. The formula for Tiron is $C_6H_2(OH)_2(SO_2ONa)_2.H_2O$. The name Tiron was adopted because of its reaction with both titanium and iron.
3. Add 50 ml of buffer solution to each beaker.	3. The solution must be buffered at pH 4.7 so that sodium dithionite reduces iron to destroy the purple ferric iron complex.
4. Use a spatula to add 10-20 mg sodium dithionite to the blank solution as well as to the standard solutions. Mix gently with stirring rods.	4. Vigorous mixing causes sulfur to precipitate.
5. Set the spectrophotometer at 430 nm and adjust to zero absorbance with H_2O. Read the absorbance of the solutions.	
6. Add dithionite powder to the next 10 beakers. One by one, stir gently, pour into the absorption cell, and measure absorbance.	6. The purple color of the iron complex fades to the yellow color of the titanium complex.

7. Repeat step 6 with the remainder of the solutions taken 10 at a time.

8. Treat the rock standards' data by the method of least squares. Calculate percent TiO_2 in the unknowns.

9. Use the data to correct apparent Al_2O_3 values as well as to report percent TiO_2.

7. A time limit between dithionite addition and absorbance reading is necessary because iron will be oxidized by air. With time, the purple color of the iron complex will reappear.

Compiled by M. Cremer

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GRAVIMETRIC ANALYSIS OF AXINITE, A BORON MINERAL

(From an unpublished method devised by Frank Grimaldi)

While axinite is a silicate mineral, boron, a major constituent, complicates the analysis of silicon, iron, and aluminum. At the beginning of the analysis, boron is removed with methanol as $B(OCH_3)_3$. Otherwise, the analysis proceeds in the usual manner. Boron is determined by elution and titration with mannitol. The following method, although written to handle small samples, can be amended when sufficient sample is available.

Procedure

1. Weigh 0.20 g sample into a small preweighed platinum crucible. Dry to constant weight at 105 ± 5°C and compute percent H_2O^-.

2. Mix the dried sample with one gram Na_2CO_3. Fuse in the usual manner.

3. Leach the crucible and its contents overnight with 25 ml H_2O in a 75 ml platinum evaporating dish. Break up the cake, remove and rinse the crucible, inspect it for adhering particles, and add with care 5 ml HCl to the covered dish. When the reaction has subsided, add 5 ml methanol.

4. Dehydrate the contents of the dish on the steam bath, breaking up lumps, until the odor of Cl^- can no longer be detected.

5. Cool. Add 1.5 ml HCl. Bring the acid in contact with all the solids. Let stand 10 minutes. Wash the sides and cover with 1:20 HCl solution. Add 19 ml H_2O, heat and dissolve the sodium chloride. Then add 5 ml CH_3OH and dehydrate again.

6. Repeat step 5 again with the exception of the addition of CH_3OH. Filter as soon as possible using 7 cm S and S black ribbon filter paper. Wash with cold 1:20 HCl and finally with hot H_2O. Use drops of 0.005 percent methyl orange on the filter paper to test for removal of acid, i.e. until the yellow color appears.

7. Return filtrate to dish. Add 5 ml CH_3OH. Evaporate to dryness. Repeat step 6, but use Munktell 00 paper and add paper pulp to the solution before filtering. Wipe dish with small pieces of hardened filter paper and add the pieces to the filter.

8. Fold both filter papers into the fusion crucible which was previously cleaned on the outside, ignited, cooled, and weighed. Ignite to constant weight at 1050°C.

9. Proceed with remainder of the analysis as set forth in Classical Analysis: The Main Portion, remembering to scale down if only 0.20 g was used. Fe_2O_3, Al_2O_3, TiO_2, MnO, CaO, MgO, the alkalies, H_2O, and FeO must be determined. A separate portion is used for boron--see Determination of Boron in Silicates.

Compiled by M. Cremer

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ANALYSIS OF A CHROME SPINEL

(from an unpublished method devised by Frank K. Grimaldi)

This method applies specifically to situations where no provision need be made to determine Mn, Ni, Zn, V, and Ti because the semiquantitative spec report shows these elements to be present at concentrations below 0.1 percent each. While the method is semi-micro, it may be altered appropriately when sufficient sample has been submitted. SiO_2 and Al_2O_3 are determined gravimetrically, while Cr and Fe are determined colorimetrically.

Reagents (all chemicals-reagent grade):

Standard Chromate Stock Solution: Dissolve 0.5656 g of dry NBS 136 $K_2Cr_2O_7$ in 2 percent w/v NaOH and make to volume with 2 percent NaOH in a 200 ml flask. 1 ml = 1000 µg Cr.

Standard Chromate solution for calibration curve: Take 10 ml of the stock solution and dilute to 100 ml with 2 percent NaOH. 1 ml = 100µg Cr.

NaOH wash solution: make 1 liter 1 percent w/v.

NaOH solution 2 percent w/v: For use in making standards, make one liter.

CHROMIUM:

Procedure

1. Fuse 0.050 g sample with 1.5 g Na_2O_2 in a zirconium crucible. Cover with a watch glass, and add 25 ml of H_2O. Let stand to disintegrate the melt, stirring occasionally. Warm if necessary, but if reaction is violent, quench the crucible quickly in cold H_2O.

2. Quantitatively transfer the contents to a 100 ml beaker. The volume at this point should be ~50 ml.

3. Digest the solution on the steam bath overnight to destroy the peroxide and to make the precipitate filterable.

4. Filter into a 150 ml beaker through a small Whatman No. 40 filter paper previously washed with 1 percent NaOH solution. Transfer and wash the precipitate with 1 percent NaOH, collecting the washes with the main solution. The volume should be about 75 ml at this point. If any $Fe(OH)_3$ passes through the filter in the colloidal state, digest the solution (covered beaker) on the steam bath until the precipitate settles. Filter again, collecting the filtrate in a 100 ml volumetric flask and washing with 1 percent NaOH solution. Make to volume with 1 percent NaOH solution.

5. Mix and reserve.

6. For the standard curve, transfer 0, 1, 3, 5, and 10 ml aliquots of the standard solution of 100 μg/ml to 100 ml volumetric flasks. Make to volume with 2 percent NaOH solution and mix.

7. Transfer 10 ml aliquots of the unknowns to a series of 100 ml volumetric flasks. Make to volume with 2 percent NaOH solution.

8. Determine the absorbance of each solution at 370 nm in 1 cm cells, using H_2O as a reference.

9. Determine the Cr content of the samples using the standard curve.

SILICA, AMMONIA GROUP, CALCIUM, AND MAGNESIUM:

Procedure	Comments
1. Sinter for 30 minutes at $500^0 \pm 20^0C$, 0.2 g sample mixed with 2 g Na_2O_2 in a small (covered) Pt crucible (~10 ml).	1. Place crucible with its contents in a cold muffle and bring to temperature.
2. Cool and place crucible in a 50 ml Pt dish. Add 20 ml H_2O, cover with a teflon watch glass, and place on steam bath to disintegrate melt and destroy peroxide.	
3. Acidify with ~3 ml $HClO_4$ and add 3 ml $HClO_4$ in excess. Remove crucible. If grains of undecomposed mineral are present, filter the solution and reserve it. The residue and paper must be ashed and resintered with Na_2O_2.	3. $HClO_4$ is used instead of HCl - see comment 4.
4. Evaporate excess H_2O on steam bath. Heat on hot plate to fumes of $HClO_4$. Add 25 ml of H_2O and heat to dissolve salts.	4. Dehydration of SiO_2 is far more complete with $HClO_4$ than with HCl. This is achieved in a single operation. The salts are mushy because $HClO_4$ does not go to dryness.
5. Filter through a 5.5 or 7 cm Whatman No. 40 paper, collecting filtrate in another 50 ml Pt dish. Wash with H_2O and transfer paper and precipitate to a small weighed ~10 ml Pt crucible. Set aside.	
6. Evaporate the filtrate on the steam bath and bring to fumes of $HClO_4$ again.	6. Filtrate contains Fe, Mg, Ca, Ni, Al, some Si, and Cr.
7. Add 25 ml H_2O. Again heat to dissolve soluble salts. Filter as before, collecting filtrate in a 50 ml beaker. Combine residue with that described in step 5 above.	
8. After ashing the papers, ignite the two residues to constant weight at 1050^0C.	8. The residue is impure SiO_2.
9. Add to the residue a few drops $HClO_4$ and a few ml HF. Evaporate the solution and fume off the $HClO_4$. Ignite and weigh.	9. $SiF_4\uparrow$. The loss in weight equals SiO_2.

10. Fuse with $K_2S_2O_7$ any residue from step 9. Keep the crucible covered and heat slightly above the melting point of potassium pyrosulfate so that few fumes of SO_3 escape. Finally, heat the crucible to low bottom redness. Cool, dissolve in a few ml H_2O acidified with a few drops HCl and add to the main solution.	10. The residue, if any, consists of those elements now in the main solution; i.e. Fe, Mg, Ca, Ni, Al, Cr.
11. Add to the main solution a few ml of H_2SO_3 to reduce Cr. Boil out the SO_2 and add 1 ml HNO_3. Boil again to reoxidize Fe.	
12. Precipitate the ammonia group by following the procedure outlined in Classical Analysis: the Main Portion-the Ammonia Group; however, scale down volumes, glassware, filter paper reagents, etc., to fit the semi-micro situation. The filtrate will be in a 150 ml beaker at this point. Digest on steam bath. Reserve the filtrate for Ca and Mg.	12. The precipitate is Cr, Fe, Al, and part of the Ni. The digestion of the filtrate will determine if any R_2O_3 crept through the filter paper. If precipitate appears, it must be filtered off and added to the rest of the R_2O_3 precipitate.
13. Dissolve the precipitate in a small excess of HCl and repeat the NH_4OH precipitation, filtration, and washing. Combine the filtrate with that of step 12.	13. If there is a delay in dissolving the precipitate, $Al(OH)_3$ may fail to completely dissolve. If the solution of the dissolved precipitate is turbid, i.e. $Al(OH)_3$ has passed through the filter paper, heat the solution on the steam bath.
14. Again dissolve the precipitate in a small excess of HCl in a 50 ml beaker. Add 2 ml $HClO_4$ and take to fumes.	
15. Add 1 ml HCl dropwise down the side of the covered beaker while fuming strongly for at least 15 minutes. Repeat the process at least four times more. If during the fuming much $HClO_4$ is lost by evaporation, add more.	15. Chromium is removed as chromyl-chloride (CrO_2Cl_2). $HClO_4$ should not be completely volatilized because chromic acid is easily reduced by HCl and must be oxidized to the hexavalent state by fuming $HClO_4$. HCl is added so slowly to permit the reoxidation of Cr to occur as quickly as possible.
16. When volatilization is complete, i.e. when the fuming $HClO_4$ fails to bring out the dichromate color, wash off cover and stirring rod, bring to fumes again. Add 25 ml H_2O and heat to dissolve salts.	16. If the solution is green, not only is Cr still present, but it is in its reduced +3 state.
17. Add 30 ml of H_2O and digest to dissolve salts. Precipitate again with NH_4OH in the usual manner. Digest again on steam bath and adjust pH again if necessary.	17. The precipitate is filterable when it clots.

18. Filter through small double filter papers (no. 41 inside 589 white ribbon), and wash with hot 2 percent NH_4Cl. Digest the filtrate. If more R_2O_3 forms, filter and combine the precipitate with the main R_2O_3 portion. Reject the filtrate.	18. See step 1. Classical Analysis: The Main Portion – the Ammonia Group.
19. Ignite the R_2O_3 to constant weight and fuse with potassium pyrosulfate. Add 1 ml HCl and H_2O to dissolve the melt.	19. Precipitate contains Fe, Al, Ni, Ti, and some Cr. Since there is little Ti and Ni, they are not determined.
20. Make the solution to 250 ml in a volumetric flask; on a 5 ml aliquot, determine Fe by o-phenanthroline.	20. See procedure for Fe by O-phenanthroline.
21. Remove a 50 ml aliquot from the 250 ml above. Neutralize with NaOH until a faint precipitate just starts to form. Discharge the precipitate with a few drops of dilute HCl.	21. Some Cr may still remain in the R_2O_3 group; it is determined spectrophotometrically as chromate.
22. Heat the above solution and pour it into 20 ml of hot 10 percent w/v NaOH containing 0.15 ml of 30 percent H_2O_2. Rinse the solution beaker with hot 1 percent NaOH.	
23. Digest the mixture for at least three hours to destroy H_2O_2 and to allow the hydroxide precipitate to form and clot.	23. The precipitate contains all the elements as hydroxides except the Cr which remains in solution.
24. Filter, discard the precipitate, and make the filtrate to 100 ml in a volumetric flask. Determine chromium as chromate.	24. See procedure for colorimetric Cr. Al_2O_3 is determined by difference in the usual manner.
25. Use the filtrate in the 150 ml beaker (steps 12 and 13) to precipitate calcium and magnesium in the usual manner (see Calcium and Magnesium-Classical Analysis: Main Portion).	25. Reagents, etc. must, of course, be scaled down to accommodate this semimicro method. Such a small amount of calcium may not precipitate. Ni, also present in the filtrate, does not precipitate with either Ca or Mg when oxalate is present.
26. If desired, isolate $CaSO_4$ after dissolving $Mg_2P_2O_7$ in the usual manner. (See Calcium Recovery from Magnesium-Classical Analysis: Main Portion).	

Compiled by M. Cremer

GRAVIMETRIC DETERMINATION OF PHOSPHORUS

When sufficient sample is available and the anticipated concentration of P_2O_5 is 3 percent or more, it is well to determine phosphorus gravimetrically as $Mg_2P_2O_7$. The sample is fused with a mixture of Na_2CO_3 and Na_2O_2, and silica is removed following acidification with HNO_3 and dehydration. The phosphorus is then separated by precipitation with ammonium molybdate, followed by dissolution with NH_4OH; then a double precipitation is made as $MgNH_4PO_4$ with subsequent ignition to $Mg_2P_2O_7$.

Reagents (all chemicals-reagent grade):

$(NH_4)_6Mo_7O_{24}.4H_2O$ (Ammonium molybdate): 30 percent (w/v) aqueous solution, filtered.

Magnesia mixture: Dissolve 50 g $MgCl_2.6H_2O$ and 100 g NH_4Cl in 500 ml H_2O. Add NH_4OH in slight excess and allow to stand overnight. Make slightly acidic with HCl, dilute to 1 liter, and store in a glass-stoppered Pyrex bottle.

Citric acid, 2 M: Dissolve 38 g citric acid in 70 ml H_2O. Dilute to 100 ml. Filter. Store in Pyrex bottle.

Procedure	Comments
1. In a covered platinum crucible, sinter a 0.5 g sample and 0.1 g SiO_2 with 1 g Na_2CO_3 and 1 g Na_2O_2 at 500°C in a muffle furnace for 1 hour. Remove from muffle and allow to cool.	1. Na_2O_2 provides an oxidizing atmosphere within the crucible, but attacks platinum at temperatures above 500°. SiO_2 is added to insure complete removal of F.
2. Add a few ml H_2O to the crucible and allow the melt to leach for a few minutes. Transfer the contents of the crucible, as completely as possible, to a large (~ 300 ml) platinum dish. Cover. Add 5-10 ml HNO_3 to the crucible, cover and let stand a few minutes to react with any of the fusion still in the crucible.	2. HCl and H_2SO_4 must be avoided as they tend to retard the precipitation of ammonium phosphomolybdate.
3. With the platinum dish covered with a watch glass, pipet 25 ml 1 + 1 HNO_3 into the dish through the spout. When reaction ceases, remove the cover and add the contents of the crucible to the dish, carefully policing and washing the crucible.	

4. Cover the dish and heat on the steam bath until reaction stops. Rinse the cover and sides of the dish with a little water. Support the watch glass with a glass triangle and dehydrate as in the usual silica determination.	4. See Classical Analysis: The Main Portion.
5. Cool the dish slightly. Add to it 10 ml concentrated HNO_3 and let stand, cold, 10 minutes. Wash cover and sides of dish with 5 percent HNO_3. Add water to about 70 ml. Cover the dish and digest on the steam bath until the salts are dissolved.	
6. Filter while still warm through 11 cm Black Ribbon paper into a 600 ml beaker. Wash dish and filter several times with 5 percent HNO_3. Then wash the filter with hot water until a drop of diluted methyl orange on the filter indicates all acid has been removed; i.e. the paper turns from red to yellow-orange.	
7. Place beaker containing the filtrate on the steam bath. Cover and keep warm several hours to destroy any pyrophosphate present.	7. Phosphate should be present as orthophosphate in order to precipitate with molybdate.
8. Place the filter containing the impure silica in the platinum crucible. Burn off the paper at a low temperature in the muffle, then ignite at 1000°C.	8. It is unnecessary to weigh the silica as it is merely being removed, not determined.
9. Treat the silica with several drops of water, 1 drop HNO_3, 3 drops $HClO_4$, and several ml HF. Evaporate to dryness on the hot plate. Fuse the remaining residue with 0.5 g Na_2CO_3. Dissolve the fusion in 5 ml HNO_3 and add to the main solution in the beaker.	9. Metal-forming phosphates slightly soluble in acid are left with the silica, and the phosphorus is recovered by driving off SiF_4.
10. Add 25 g NH_4NO_3, dilute to 300-400 ml and stir to dissolve all the nitrate. Add HNO_3 as necessary to make the solution 5 percent in HNO_3.	10. In the next step, phosphorus will be separated from interfering elements by precipitation as ammonium phosphomolybdate in acid medium prepared in this step.

11.	Heat the solution to approximately 90°C. While stirring, add 100 ml ammonium molybdate solution. Remove from heat. Stir frequently until cool and let stand overnight.	11.	Quantity of molybdate solution given is for samples containing ~ 50 percent P_2O_5. Less should be used if P_2O_5 concentration is expected to be less--down to 20 ml for 3 percent P_2O_5.
12.	Filter through 15 cm Whatman No. 42 paper, collecting filtrate in 800 ml beaker. Wash precipitate thoroughly with 2 percent HNO_3. It is not necessary to police the precipitation beaker at this time.	12.	A yellow precipitate of ammonium phosphomolybdate forms which may also contain some white precipitate of molybdic acid. Yellow filtrate indicates incomplete removal of silicon. These occurrences are unimportant.
13.	When the filter has thoroughly drained, wash the precipitate from the funnel with water back into the 600 ml precipitation beaker. Place the beaker under the funnel.		
14.	Dissolve the precipitate by washing around the edge of the filter with dropwise application of 1 + 2 NH_4OH, collecting the washings in the 600-ml beaker containing the precipitate. Wash the filter paper five times with 5 percent NH_4OH, then several times with hot water, finally with 5 percent HCl. If the paper turns yellow after the HCl washing, the entire 1 + 2 NH_4OH, water, 5 percent HCl cycle is repeated until the paper remains white.	14.	All the precipitate will eventually dissolve in the NH_4OH.
15.	With the paper acid to HCl, add through the paper 2 ml of 2M citric acid solution. Using methyl red as indicator, make the filtrate slightly acid with 1 + 1 HCl. Reserve filter paper. Heat the filtrate on the steam bath for two hours to allow the Al and Fe to complex.	15.	Citric acid is added to complex the Al and Fe, which will occur only if the solution is acidic. Phosphomolybdate may reprecipitate as the solution is acidified, but this should not alarm the analyst.
16.	Add a few drops of methyl red, then add 1 + 1 NH_4OH until alkaline and all the precipitate has dissolved.	16.	Heat of the steam bath encourages the precipitate to dissolve. If molybdic acid (white) has precipitated, a little more time on the steam bath, with occasional stirring, will be necessary.
17.	If, when the solution is warm and alkaline, it still has solid material in it, filter it through the same No. 42 paper. Wash well with 5 percent NH_4OH and ignite the paper in the platinum crucible. Fuse any residue with 0.5 g Na_2CO_3, extract the melt with H_2O, filter, acidify with HCl, and add to main solution.	17.	The phosphorus in such insoluble phosphates as those of titanium and zirconium is converted into sodium phosphate.

18.	Adjust volume of the solution to 200-300 ml. Render slightly acid with 1 + 1 HCl.	18.	Evaporation or dilution may be necessary. Solution must be acid before addition of Magnesia mixture.
19.	Add 10 ml Magnesia mixture plus 0.1 ml more for every mg of P_2O_5 expected. Stir during addition.	19.	If sample is pure apatite, 50 ml Magnesia mixture will be needed.
20.	While stirring, make the solution alkaline with slow dropwise addition of 1 + 1 NH_4OH. After the precipitate has formed, add NH_4OH to 10 percent of total sample volume. Stir occasionally. Let stand overnight.		
21.	Filter through a 12.5 cm Blue Ribbon paper. Wash well with 5 percent NH_4OH.		
22.	Wash the precipitate with water from the paper into a 250 ml beaker. Replace the paper in the funnel with the 250 ml beaker beneath it. Wash the precipitation beaker with 25 ml 1 + 1 HCl, then pour directly into the 250 ml beaker. Rinse the precipitation beaker several times with hot 5 percent HCl, pouring the rinsings through the filter. Wash the paper well with hot 5 percent HCl; finally wash with water two times. Discard filter paper. Volume in the 250 ml beaker should be about 100 ml.		
23.	Add a few drops of methyl red, then add 1-2 ml Magnesia mixture. Stir well while making alkaline as before with 1 + 1 NH_4OH. Stir well and add NH_4OH very slowly during the precipitation.	23.	Precipitate should form very slowly and be crystalline. If solution looks murky and cloudy during precipitation, add more HCl to acidity, then add ammonia again.
24.	Let stand for an hour or more with occasional stirring. Add NH_4OH to a concentration of 5-10 percent as before and let stand overnight.		
25.	Filter through 12.5 cm No. 42 paper and wash well with 5 percent NH_4OH.		

26. Place filter in a weighed platinum crucible. Burn off the paper at as low a temperature as possible in the muffle. Finally, when carbon is all removed, ignite at 1100° to $Mg_2P_2O_7$. Cool in desiccator and weigh. Repeat ignitions until constant weight is obtained.

Calculations:

$$\text{Percent } P_2O_5 = \frac{\text{wt. } Mg_2P_2O_7 \times 0.63774 \times 100 \text{ percent}}{\text{weight sample}}$$

Compiled by S. Neil

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MAIN PORTION ON PHOSPHATE ROCKS AND MINERALS

(Procedure adapted from E. F. Cruft, C. O. Ingamells, and J. Muysson, Geochimica et Cosmochimica Acta, 1965, v. 29, p. 581-597.)

Gravimetric analysis of rocks and minerals containing more than 1 percent P_2O_5 is best accomplished by using separate portions each for silica, phosphorus, and the remaining main constituents. The following procedure describes the separation and determination of other main constituents after the determination of silica and phosphorus. The sample is fused with Na_2CO_3 and Na_2O_2, silica is removed and discarded, and phosphorus is removed with zirconyl chloride prior to precipitation of the R_2O_3 group, which is later analyzed by chemical methods.

Reagents (all chemicals-reagent grade):

Zirconyl chloride solution: Weigh and transfer 9-10 g $ZrOCl_2 \cdot 8H_2O$ to a 500 ml volumetric flask. Dilute to volume with H_2O. After several days, filter the solution into a Pyrex bottle for storage. Standardize the sollution as follows: Remove a 25 ml aliquot and precipitate $Zr(OH)_4$ with NH_4OH as in the usual R_2O_3 group separation. Reprecipitate after dissolution in HCl. Filter. Place filter and precipitate in a weighed Pt crucible, char the paper, and ignite to constant wt at 1000°C. Calculate the concentration of the solution in mg/ml ZrO_2.

Procedure	Comments
1. Determine H_2O^- on a 1.0 g sample, then mix with it 0.2 g specpure quartz, 4 g Na_2CO_3, and approximately 0.5 g Na_2O_2. Fuse in the usual manner over a strongly oxidizing Meker flame. Cool.	1. Quartz is added to make the volatilization of fluoride more complete. It is unnecessary to add it if silica content of the sample is known to exceed 5 percent.
2. Transfer the fusion to a Pt dish with H_2O. Add about 5 ml 1+1 HCl to the covered dish containing the fusion. Let stand overnight. Add the HCl from the crucible, then carefully wash and police it, adding the washings to the dish. Carefully wash the crucible with water, ignite, cool and weigh it, then set it aside for later use.	
3. Heat the covered dish on the steam bath until effervescence ceases. Then rinse the cover and sides down and remove and reserve the cover.	
4. Allow to evaporate, UNCOVERED, to dryness. Dehydrate overnight on steam bath.	4. Fluoride must be entirely removed, as its presence interferes with complete precipitation of Al. Removal of F- is more thorough if dish is completely uncovered.

5. Remove dish from steam bath and allow to cool. Take up the salts in 10 ml concentrated HCl. Let stand 10 minutes. Wash down sides of dish with 5 percent HCl and add water to a total volume of 50-70 ml. Heat, covered, on steam bath until salts are dissolved and solution is hot.	
6. Filter through 11-cm Black Ribbon paper, catching filtrate in a 600 ml beaker. Wash several times with 5 percent HCl, then with hot water until diluted methyl orange shows that all acid has been removed.	6. Diluted methyl orange (~0.005 percent) is applied dropwise to upper edge of filter after it has drained. Pink color denotes presence of acid; if acid has been removed, the indicator will be pale yellow. Samples in which phosphorus is high create greater difficulty in complete removal of HCl (due to formation of phosphoric acid).
7. When filter has completely drained, place the paper in the reserved crucible and set aside. Return the filtrate to the dish and dehydrate two more times on the steam bath. After each dehydration, take up the salts in HCl as before and during the filtration of the silica, add a pinch of filter pulp. Filter through Whatman No. 40 or Muntell's 00 paper. Wash thoroughly as before.	
8. Place all filters in the Pt crucible, then burn them off at a low temperature and ignite the silica. No need to weigh the silica.	8. Silica is merely being removed, not determined.
9. Moisten silica with a few drops of water. Add 3 drops $HClO_4$, 2 drops HNO_3, and half fill the crucible with HF. Evaporate to fumes on a hot plate. Add several drops of water, pack the crucible half full of paper pulp, and add a few ml NH_4OH. Place in cold muffle, burn off paper at a low temperature, then ignite to red heat of muffle. Cool. Fuse residue with 0.5 g Na_2CO_3. Dissolve fusion in 10 ml 1+1 HCl and add to the filtrate from the silica.	9. While silica is being ignited and volatilized, heat the filtrates, covered, on the steam bath for several hours to convert any pyrophosphate present to orthophosphate.
10. Heat the solution on the hot plate to a temperature of about 90°. Volume of the solution should be about 200 ml, and it should contain about 10 percent HCl.	

11. From the known concentration of P_2O_5, calculate the quantity of a standard solution of $ZrOCl_2$ which must be added to react with the P_2O_5. Slowly add enough of the $ZrOCl_2$ from a burette to the hot solution to theoretically precipitate the phosphorus, plus an excess of approximately 10 mg ZrO_2.	11. The ratio is Zr:2P. See Hillebrand, et al, p. 569-571.
12. Place the beaker on the steam bath and heat it for 20-30 minutes, stirring occasionally.	
13. Filter through a 12.5 cm Whatman No. 541 paper folded inside a Blue Ribbon paper, catching filtrate in a 1000 ml beaker. Wash the precipitate superficially with 5 percent HCl.	
14. Return the filtrate to the precipitation beaker, using as little water as possible. Add 20 ml concentrated HCl, cover the beaker, and heat on the steam bath for 30 minutes to an hour. Add water to make a volume of about 200 ml.	14. The Zr phosphate is an extremely bulky precipitate, and it would be very difficult, if not impossible, to wash it thoroughly in the funnel in the usual way.
15. Filter again through the same paper, catching filtrate in the same beaker as before. Wash superficially with 5 percent HCl as before. Repeat steps 14 and 15 two more times.	
16. The zirconium acid phosphate (presumed to be of the composition $ZrO(H_2PO_4)_2$) may be placed in a large Pt crucible, carefully ignited to ZrP_2O_7, and analyzed, if desired. For specific instructions, see Cruft et. al, p. 594.	16. $ZrOCl_2 + 2H_3PO_4 \longrightarrow ZrO(H_2PO_4)_2 + 2HCl$.
17. Evaporate the filtrate to a volume of about 250 ml in 400 or 600 ml beaker.	17. If more Zr phosphate precipitates during the evaporation, it may be ignored.

18. Add approximately 60 ml NH_4OH. Heat solution to boiling and precipitate the R_2O_3 group by addition of NH_4OH to pH 6.4 as usual. Filter through an 11 cm Whatman No. 41 paper folded inside an S. and S. White Ribbon paper, collecting filtrate in an 800 ml beaker. Wash thoroughly with hot 2 percent NH_4Cl as usual.	18. It is unnecessary to add any additional NH_4Cl, as sample already contain a large volume of HCl.
19. Transfer precipitate back into the precipitation beaker and to it add 10 ml HCl. Heat until precipitate dissolves, then reprecipitate, filter, and wash as described in "Classical Analysis, Main Portion." Place the filter and precipitate in the crucible in which the original fusion was made. Burn off the paper at a low temperature, then ignite at 1000°. Weigh.	19. The weight of the mixed oxides is meaningful only to the extent that it is of use to the analyst in determining the quantity of $K_2S_2O_7$ to use in a first step of the extended analysis of the R_2O_3 precipitate (described at the end of this section).
20. The combined filtrates from the R_2O_3 group should be evaporated to approximately 300 ml in a 600 ml beaker. If the filtrate is not acid to methyl red following the evaporation, add 1:1 HCl dropwise to the red color, then add about 10 drops in excess.	
21. To the boiling filtrate, add 40 ml 10 percent oxalic acid. Remove from the burner and place the beaker on the steam bath. Add NH_4OH slowly, dropwise with stirring until precipitate starts to form. Then stir occasionally as precipitate is forming and settling to the bottom, adding NH_4OH only as the precipitate assumes a heavy, crystalline form.	
22. Finally add NH_4OH until the methyl red has turned yellow and pH of the sample is slightly higher than 6.	22. The pH may be checked by dipping a small piece of indicator paper into the solution and observing the color.
23. Digest the sample on the steam bath for 1-2 hours, stirring occasionally. Then remove from heat and let stand overnight.	

24. Filter through 11 cm Whatman No. 42 paper into a 1000 ml beaker. Wash carefully with 0.1 percent $(NH_4)_2C_2O_4$.	
25. Using water, rinse the precipitate from the paper back into the beaker in which the precipitation was made. Return the paper to the funnel. Rinse the walls of the beaker with hot 5 percent (v/v) HCl, add 10 ml 1:1 HCl, cover the beaker, and heat on steam bath until the precipitate is dissolved.	25. Calcium oxalate does not readily dissolve in very dilute HCl, therefore 1+1 HCl must be used for dissolution of the major part of the precipitate.
26. Replace the 1000 ml beaker under the funnel with a 400 ml beaker. When all the precipitate has dissolved, carefully pour the liquid through the filter and collect it in the 400 ml beaker. Wash paper thoroughly with hot 5 percent HCl, then several times with water. Reserve the paper.	
27. Adjust the volume of the liquid to ~200 ml and add 3-4 drops of methyl red. Bring the solution to a boil and add NH_4OH dropwise until precipitate starts to form. Remove beaker from burner and place on the steam bath. Add NH_4OH slowly, dropwise, with stirring as in steps 21 and 22. Omit any further addition of oxalic acid until precipitation is complete, then add 1 ml oxalic acid, and adjust to pH 6 as before.	
28. Digest on steam bath until precipitate has settled well, then remove to stand before filtration within 3-4 hours.	28. The second precipitate of calcium oxalate should be filtered after 3-4 hours as post-precipitation of magnesium will occur after longer standing.
29. While the calcium precipitate is awaiting filtration, dissolve 7 g $(NH_4)_2HPO_4$ in a small amount of water. Pour the solution through the No. 42 paper, catching it in the beaker containing the filtrate from the first calcium precipitation.	
30. Filter the calcium oxalate through a new No. 42 paper, wash well with 0.1 percent ammonium oxalate, and collect the filtrate in the 1000 ml beaker.	

31. Transfer the paper to a weighed platinum crucible. Ash at a low temperature, then ignite to $CaCO_3$ at 475-500°C. Cool. Ignite, weigh, and calculate percent CaO.	31. $CaCO_3$ should be dissolved in HNO_3 and checked for presence of Mn as in "Classical Analysis, the Main Portion."
32. To the filtrate from step 30, add NH_4OH in the amount of 10 percent of its volume. Cover and let stand for several days, stirring several times each day.	
33. Filter $MgNH_4PO_4$ through an 11 cm Blue Ribbon paper, washing well with 5 percent NH_4OH. Dissolve the precipitate by washing with hot 5 percent HCl and catching the washings in a 150 or 250 ml beaker.	33. If MgO is known to exceed 20 percent (unlikely in phosphate samples), the second precipitation should be made in a volume of 200 ml or more.
34. Add 1.5-2 ml 15 percent NH_4Cl for every 10 mg MgO that is expected. Add 2-3 drops methyl red.	
35. Add NH_4OH <u>very</u> slowly dropwise, with stirring. Do not strike the walls of the beaker with the stirring rod. Continue the addition of the ammonia until the methyl red has turned yellow and precipitation appears to be complete.	35. Precipitate should form large crystals. If the liquid takes on a cloudy appearance, stop the addition of the ammonia. Make the solution acid again with HCl and begin the addition of NH_4OH again.
36. Cover and let stand for about 30 minutes, stirring occasionally. Add ammonia in the quantity of 10 percent of the volume present.	
37. Let stand for an hour or more, then add 1 ml of 25 percent $(NH_4)HPO_4$, stir and cover to stand overnight.	37. Precipitation is facilitated if, each time the solution is stirred, the walls of the beaker are washed down with 5 percent NH_4OH in such a manner that a thin layer of ammonia floats on top of the solution.

38. Filter through a No. 42 Whatman paper, combining the filtrate and washings with those from the first Mg filtration. Wash the precipitate thoroughly with 5 percent NH_4OH.

39. Transfer the filter to a pre-weighed platinum crucible. Place the uncovered crucible in a cold, well-ventilated muffle furnace. Carefully char and burn off the filter paper at as low a temperature as possible, then ignite at 1100°C until carbon is completely removed.

40. Cool and weigh the $Mg_2P_2O_7$. Repeat ignitions until constant weight is attained. Correct the weight by subtracting the Ca and Mn present. Then calculate $Mg_2P_2O_7$.

40. The $Mg_2P_2O_7$ should be dissolved in H_2SO_4 and calcium and manganese determined as described in "Classical Analysis, the Main Portion."

Compiled by S. Neil

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EXTENDED ANALYSIS OF THE AMMONIA GROUP PRECIPITATE

(Adapted from an unpublished method devised by C. O. Ingamells)

In rock analysis, it is customary to determine alumina by difference, by subtracting the weights of all other ammonia group constituents from the total weight of the ammonia group. That which remains is assumed to be Al_2O_3. Occasionally, however, it is necessary to do an extended analysis of the R_2O_3 group, thereby determining alumina directly by precipitation of aluminum phosphate. This extended analysis may be necessary whenever unusual constituents or contaminants are expected to accompany the R_2O_3 group, such as when zirconium has been added to remove phosphate.

Procedure	Comment
1. Add to the ammonia precipitate twenty times its weight of potassium pyrosulfate. Heat over an oxidizing flame until the entire precipitate appears to have dissolved. Set the crucible on a porcelain plate to cool.	1. See step 19, Main Portion on Phosphate Rocks and Minerals.
2. Add to the fusion 10 ml water. When the fusion cake has loosened from the crucible, transfer the crucible contents to a 250 ml beaker, thoroughly washing and policing the crucible. Add 10 ml 1+1 H_2SO_4.	
3. Heat beaker and its contents on the steam bath, evaporating, if necessary, to a volume of ~50 ml. When the fusion cake has dissolved, filter the solution through a 9 cm Black Ribbon paper, collecting filtrate in a 250 ml beaker. Wash filter carefully with 1 percent H_2SO_4.	
4. Place the filter in the platinum crucible in which the pyrosulfate fusion was made. Burn off the paper at a low temperature in the muffle furnace as usual, then ignite at 800°.	
5. When the crucible has cooled, add 2 drops of 1+1 H_2SO_4 and 10 drops HF. Place on a clean hot plate and heat at <100°C until HF is removed, then increase temperature and heat to fumes of SO_3. Fuse the residue with a little pyrosulfate, take up the fusion in 10 percent H_2SO_4 and add to the main solution.	

6. Wipe off the crucible, ignite, and weigh it. Reserve crucible for later use.

7. Adjust the volume of the main solution to ~100 ml. Add to it enough of a 50 percent NaOH solution to nearly, but not quite, neutralize the free acid.

8. Heat almost to boiling (~80°C) and rapidly pour it into a large (250-350 ml) platinum dish which contains enough NaOH to give a final concentration of 1 percent NaOH. Again, heat nearly to boiling, then digest on the steam bath for an hour. Let stand until cool.

9. Filter into a 800 ml beaker through a Whatman No. 541 paper folded inside a Blue Ribbon paper. Wash the precipitate with a solution which is 1 percent in NaOH and in Na_2SO_4.

10. Remove the hardened paper without disturbing the other and sluice the precipitate from it back into the large platinum dish. Replace the filter in the funnel and wash it thoroughly with 5 percent HCl, catching the washings in the original 250 ml beaker.

11. Add 5 ml concentrated HCl to the precipitate to dissolve it, heating if necessary. Pour it through the filter, into the 250 ml beaker, then thoroughly wash the dish and filter with water until free of acid.

12. Nearly neutralize with a 50 percent solution of NaOH, heat to near boiling, then pour it into enough hot 20 percent NaOH in the platinum dish to make a final NaOH concentration of 3 to 5 percent.

13. Cover the dish at once, heat to boiling, and boil for a minute or two. Remove from heat and let stand overnight to cool thoroughly.

8. Be sure to add the sample solution rapidly to the NaOH, as a better precipitate will result.

9. The precipitate will consist of hydroxides of iron, titanium, zirconium, and the rare earths. The filtrate contains the aluminum.

11. The analyst should keep a record of the volume of HCl used, so that the amount of NaOH needed in the next step may be easily determined.

14. Filter through the same paper as before, combining the filtrate with the first filtrate contained in the 800 ml beaker. Wash with cold 1 percent NaOH containing 0.1 percent each of Na_2CO_3 and NaCl.

15. Place the filters in the weighed platinum crucible, burn the papers off in the muffle furnace, and ignite at 800°.

16. Make the filtrates just acid to methyl orange with 1+1 HCl and adjust the volume to 300-350 ml. Add 1-2 g of diammonium phosphate, and then 1-2 ml HCl in excess.

17. Stir in a one cubic inch portion of filter pulp, heat to boiling, and add to the boiling solution 10 g of ammonium acetate dissolved in a small amount of H_2O. Boil for 3-4 minutes then filter while hot through an 11 cm Whatman No. 40 paper. Wash superficially with warm 2 percent NH_4Cl solution. Do not let the paper run completely dry during washing and do not overwash.

18. Sluice the precipitate back into the beaker with water, add 1-2 drops methyl orange, then 1+1 HCl dropwise until the solution is acid to methyl orange.

19. Dilute to about the same volume as before and add 0.5 g diammonium phosphate. Bring to a boil and add 10 g ammonium acetate as before.

20. Boil for 2-3 minutes, then filter while hot through the same filter paper. This time the precipitate should be washed with hot 5 percent NH_4NO_3 until a portion of the filtrate gives a negative test for chloride.

21. After the filter has thoroughly drained,, place it in a preweighed platinum crucible. Slowly burn off the paper as usual, then ignite the precipitate to constant weight at 1000°C and weigh $AlPO_4$. Calculate percent Al_2O_3.

15. It is not necessary to weigh the precipitate, but it should be reserved for determination of iron and titanium. See step 22.

20. To test for chloride, add 3-4 drops 0.2N $AgNO_3$ to a small test tube. Mix with several drops of filtrate from the funnel stem. If chloride is present, a slight cloudiness will occur in the test tube due to formation of AgCl.

22. The sodium hydroxide precipitate from step 15 contains iron, titanium, and zirconium oxides. It may be fused with twenty times its weight of potassium pyrosulfate and dissolved as in steps 1-5.

23. Adjust the volume of the solution to ~75 ml in a 100 ml volumetric flask. Determine titanium colorimetrically by adding 3-5 ml 30 percent H_2O_2, then making the sample to volume. Read at 410 nm, recovering all the solution for removal of platinum and determination of total iron.

24. Evaporate the solution in a 250 ml beaker to fumes of SO_3 and fume briefly to destroy the peroxide. Add water to about 70 ml, then add Zn to remove the platinum as discussed in "Classical Analysis-The Main Portion."

25. Determine total iron by titration as follows: Evaporate the sample solution to fumes of SO_3, then increase the heat and fume briefly to rid the sample of any organic matter. Cool.. Add water to a volume of 70-80 ml and transfer the solution to a 400 ml beaker. Add 5 ml concentrated HCl and a few glass boiling beads.

26. Heat the solution to boiling, then remove from heat. Add dropwise the $SnCl_2$ solution described in comment No. 25 until the solution turns from yellow to colorless, then add only 1-2 drops more.

27. Cool the solution to room temperature (~25°C), then quickly add 10 ml of a 5 percent solution of $HgCl_2$. Do not allow the sample to stand longer than 2-3 minutes. Add enough water to make the volume ~200 ml.

23. A standard solution of titanium may be prepared from NBS standard sample no. 154 as directed by Hillebrand, et al, p. 582.

25. Total iron is determined by reducing all the iron to the ferrous (+2) state with stannous chloride, then titrating with 0.1 N $K_2Cr_2O_7$. The reaction is: $2Fe^{+2} + Sn^{+4} \rightleftarrows 2Fe^{+3} + Sn^{+4}$. Stannous chloride solution should be prepared fresh by dissolving 15 ml $SnCl_2 \cdot 2H_2O$ in 100 ml 1:2 HCl.

27. Mercuric chloride is added to oxidize any excess stannous ion. The reaction is: $2Hg^{+2} + Sn^{+2} \rightleftarrows Sn^{+4} + 2Hg^{+1}$. A silky white precipitate will form.

28. Add 5 ml concentrated H_3PO_4 and several drops of diphenylamine sulfonate indicator and titrate with 0.100 N $K_2Cr_2O_7$ to a purple end point. Calculate percent total Fe as Fe_2O_3.

$$\frac{ml_{K_2Cr_2O_7} \times N_{K_2Cr_2O_7} \times 79.85 \times 100}{\text{wt. sample in mg}} = \text{Percent } Fe_2O_3$$

79.85 is the milliequivalent weight of Fe_2O_3 expressed in milligrams.

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Compiled by S. Neil

CLASSICAL ANALYSIS: THE MAIN PORTION

The analysis consists, for the most part, in the separation and measurement by weighing of the major oxides contained in a silicate rock. These constituents are SiO_2, Al_2O_3, Fe_2O_3, FeO, TiO_2, P_2O_5, MnO, MgO, CaO, Na_2O, K_2O, and total H_2O. Procedures for FeO, Na_2O, K_2O, and total H_2O are set forth in separate sections.

The analysis begins with sample drying. Loss in weight is recorded as H_2O^-. After sodium carbonate fusion, silica is removed by HCl dehydration and is determined by volatilization with HF. Aluminum, calcium, and magnesium are successively precipitated with ammonia, oxalate, and phosphate; and ignited and weighed as oxide, carbonate, and pyrophosphate respectively. Iron, titanium, and phosphate are each determined on separate portions. Because they are found in the ammonia group precipitate, they must be subtracted to obtain Al_2O_3 by difference. Manganese, which is found in the filtrate from the ammonia group, may be separated therefrom with persulfate; or it may be recovered later from the ignited magnesium and calcium precipitates.

In addition to the aforementioned oxides, certain minor constituents may occur in some rocks. In the event of their determination or in their absence, an acceptable summation should lie between 99.8 and 100.3 percent. While a summation so near 100 percent does not guarantee a correct analysis, an unsatisfactory high or low summation is definite proof of error.

CLASSICAL ANALYSIS: THE MAIN PORTION
(From an unpublished method devised by C. O. Ingamells)

Procedure	Comments
H_2O^- and Fusing:	
1. Weigh a 25-ml platinum crucible and cover. Add to the crucible 0.700 or 0.800 gram of thoroughly mixed sample.	1. See section on the care and use of platinum. Also see section on the mixing of samples.
2. Heat the uncovered crucible for 2 hours in an oven at 105° ± 5°C. Place covered crucible in a desiccator for 30 minutes; then weigh covered crucible and contents. Repeat the foregoing until constant weight is attained.	2. Constant weight = ± 0.2 mg.
3. Place the covered crucible in a cold furnace; slowly bring the temperature to 450-500°C, then remove the lid and heat for a further 30 minutes.	3. Carbon, organic matter, or sulfides attack platinum during fusion. With samples containing no sulfide, little water, no oxidizable iron, and no carbonate or organic matter, or if the sample is likely to fuse or sinter at the low temperature used, roasting may be omitted. The preliminary heating is done with the crucible closed because sulfur, the most common volatile, is more completely removed in this way. The final heating with the crucible open results in the oxidation of iron, which is much less likely to cause trouble when it is in the ferric condition. Among materials which have been observed to volatilize on the crucible lid, under the conditions described, are metallic chlorides, arsenic compounds, thallium compounds (sometimes encountered in the analysis of minerals which have been separated using Clerici solution), sulfur and selenium compounds, ammonium salts, silica (if fluoride is present), boron compounds, and mercury.

4. Place the cool crucible on a porcelain plate and mix 3 out of 4 grams anhydrous sodium carbonate with the rock powder using a small platinum rod. Rotate the stirring rod in the remaining gram of Na_2CO_3 and transfer the latter to the crucible covering the mixture as evenly as possible.	4. The Na_2CO_3 should be free of Mg, Ca, and heavy metals. If much ferrous Fe or Mn is suspected, ~0.1 gram Na_2O_2 should be added.
5. Cover the crucible and heat very slowly over a Meker burner, gradually increasing the oxidizing flame over a period of about 20 minutes until the mixture begins to sinter. Finally increase the temperature to a bright red heat for 5-10 minutes, or until inspection of the fused mass shows no reaction. When the melt is quiet, heat the top of the crucible and the lid for a minute with a separate oxidizing flame to melt the small spatters of flux on the lid and sides. Remove the lid, invert it, and lay it on the porcelain plate; pick up the crucible and swirl or tip it so that the melt solidifies in a cup shaped layer on the walls. Cover the crucible and cool on the porcelain plate. Reheat briefly over a Meker burner until the bottom appears dull red–~30 seconds. Cool on the porcelain plate.	5. An oxidizing flame is obtained by replacing the platinum with a nickel crucible of the same size. If the red hot crucible is filmed with oxide, the flame is sufficently oxidizing: if a bright surface appears, the burner should be adjusted for more air. An oxidizing flame must be maintained at all times; failure to do so will result in reduction of iron and its deposition in the platinum.
A. If platinum dishes are used:	A. If platinum dishes are used:
1. Add about 5 ml of water to the crucible containing the melt and allow it to stand for several minutes. Stir gently with a silica rod to loosen the melt; transfer the contents of the crucible as completely as possible to a 300 ml platinum dish. Scrub the crucible with a policeman using a total of about 30 ml of water.	1. The solution of the melt and the dehydration of silica may be accomplished either in platinum dishes or in 250 ml porcelain casseroles. The use of platinum with samples high in iron, chromium, or manganese results in the introduction of large amounts of platinum; e.g. $Pt + 4\,Fe^{+3} + 6\,Cl^{-} \rightleftarrows PtCl_6^{=} + 4\,Fe^{+2}$ The use of porcelain results in the introduction of about 0.1 percent SiO_2, although the gain may be counterbalanced by the small loss due to the tenacious adherence of silica to porcelain. For higher accuracy, platinum is recommended. Silica rods are used because HCl may leach calcium from soft glass.

2. Add 5 ml of concentrated hydrochloric acid to the crucible, cover it, and set it on the porcelain plate. Cover the dish with a watch glass. If any manganate (evidenced by a green color) is present, add a few drops of ethanol. Allow the melt to disintegrate overnight. The liquid volume should not be more than about 60 ml.	2. Ethanol reduces tetravalent manganese which would subsequently react with HCl to form chlorine, which in turn severely attacks platinum.
3. Crush the residue with the rod and look closely for gritty particles which may indicate incomplete decomposition.	3. If unattacked material is present, it may be best to start over, perhaps regrinding the sample to pass a finer mesh, or fusing for a longer time. Some minerals such as zircon, chromite, sillimanite, kyanite, magnetite, ilmenite, tourmaline, beryl dissolve with difficulty in the melt. (Decomposition Techniques in Inorganic Analysis by Dolezal, Povondra and Sulcek, p. 91-103.)
4. With the dish covered, pipette approximately 15 ml of concentrated HCl through the spout. When the CO_2 has evolved, add the contents of the crucible, scrubbing and washing it thoroughly. Transfer the covered dish to the steam bath until bubbles are no longer observed. Wash down the sides of the dish and cover glass with 1:20 HCl; raise the cover on a silica glass triangle to permit evaporation.	4. Samples which contain fluorine should not be covered with glass.
5. Stir at intervals to prevent the formation of large NaCl crystals. As the residue dries, carefully crush it to a powder with the rod.	5. Silica glass rod ends must be thoroughly rounded or silica chips may be added to the sample. Teflon covered metal rods may be used if they prove to be leak proof after soaking for sometime in concentrated HCl.

B. If porcelain casseroles are used:

1. Remove melt from the crucible as described in A.1 above. Add the 5 ml of concentrated HCl to the crucible as stated in A.2 above.

2. Immediately add 15 ml HCl to the casserole as described in A.4. Let stand for several hours or overnight and then add the contents of the crucible.

3. When the melt has disintegrated, heat the covered casserole on the steam bath until CO_2 is no longer evolved. Crush the soft lumps of hydrous silica with the rod, raise the cover on a glass triangle, and evaporate as described above, stirring frequently.

4. Examine the crucible closely for contamination. Heat it for several hours in a furnace at about 800°C, or over a strongly oxidizing flame, and examine it for the purple stain characteristic of iron. If this appears, add hydrochloric acid to the crucible and heat it, covered, to dissolve the iron oxide stain. Reserve the solution so obtained for addition to the filtrate from the silica. Repeat the heating and leaching until no more iron can be recovered.

B. If porcelain casseroles are used:

3. Because dehydration of silica is more difficult in porcelain, it is particularly important to prevent the formation of crusts and large crystals of salt.

4. Because porcelain is chosen for samples high in iron, examination of the fusion crucible is more important.

Silica

1. Continue to heat the platinum dish or porcelain casserole on the steam bath until the odor of hydrogen chloride can no longer be detected after covering the dish for several minutes and then raising the cover. HCl removal may take several hours and may be continued overnight.	1. See Quantitative Chemical Analysis by Kolthoff, Sandell, Meehan, Bruckenstein, 4th edition, pp 650-661, for discussion of silica. See also Systematic Analysis of Silicates by Lee C. Peck, Geological Survey Bulletin 1170, pp 21-26. Filtration will be slow, recovery will be incomplete, and high values for alumina will result if dehydration is incomplete. The temperature should not exceed 100° C else some of the silica will become pseudo-soluble by interaction with the basic magnesium chloride formed in the dehydration.
2. While waiting for the above, carefully clean the outside of the crucible, ignite for 1/2 hour at 1000°C, cool in a desiccator, and weigh. The crucible should be free from stain or discoloration of any kind and weigh 0.1 to 0.3 milligram less than before fusion. If the loss is large--more than 1 or 2 milligrams--the platinum introduced into the analysis must be removed.	2. The clean ignited crucible will be used to ignite SiO_2 and the R_2O_3 group.
3. Cool the platinum dish or porcelain crucible; carefully add 6-15 ml of concentrated hydrochloric acid. Allow to stand for 10 minutes. If titanium is known to be low, the smaller volume of acid should be used. Wash down the cover and the sides of the dish or casserole with 1:20 hydrochloric acid, add water to a volume of 50-70 ml, and heat on the steam bath with stirring until all the sodium chloride is dissolved--30 minutes if necessary. Add more water only if necessary. Filter as soon as possible through a 9 or 11 cm S and S black ribbon paper, and wash with cold 1:20 hydrochloric acid, scrubbing the dish and transferring as much as possible of the silica to the paper. Finally wash free of acid with hot water. The progress of the washing can be followed by adding a drop of very dilute (0.005 percent) methyl orange solution to the precipitate in the paper from time to time. As long as it shows a pink color, washing should be continued.	3. Ti, Fe and Al form hydrolyzable salts. Therefore, concentrated HCl is used and is diluted after a short period of contact. Failure to wash alkali salts out of the silica results in the weighing of chlorides as well as silicates and the conversion to sulfates during subsequent treatment. The error in SiO_2 is negative; in Al_2O_3, it is positive. Difficulties in the ignition of silica to constant weight are usually due to incomplete washing.

4. Reserve the filter containing the silica. Return the filtrate to the dish or casserole and evaporate to dryness as before, stirring to prevent formation of large crystals of sodium chloride. Dehydrate overnight. Finally take up the residue in 6-15 ml of concentrated hydrochloric, let stand for 10 minutes, add water, and warm to complete solution of salt. Add a little paper pulp to the solution, stir thoroughly, and filter through a Munktell 00 or Whatman No. 40 7 or 9 cm paper. Wash thoroughly with 1:20 hydrochloric acid, scrubbing the dish or casserole very carefully with the aid of small pieces of hardened filter paper; then wash free of acid with hot water, using methyl orange indicator as before.

5. Transfer the papers containing the silica to the same crucible that was used for fusion. Burn off the paper at 200°C and ignite the silica at 1050°C for one hour. Desiccate, cool, weigh, and reignite at 30 minute intervals to constant weight.

4. Cloudy filtrate from the silica is due to the hydrolysis of Ti. If the washing of the silica is skillfully done, the volume of the filtrate will not much exceed 100 ml., even after the intensive washing necessary to remove all hydrochloric acid.

5. Heating must begin from a cold oven under strongly oxidizing conditions (an open window at each end of the oven). Not until all carbon is gone should the temperature be raised much above 450°C. Failure to attain a constant weight after several hours of heating is an indication that alkalies are present and are slowly volatilizing. It is also possible for platinum crucibles to lose weight on prolonged heating at high temperatures. See Quantitative Chemical Analysis by Kolthoff, Sandell, Meehan, Bruckenstein, 4th edition, p. 456.

6. When constant weight has been attained, add enough water to the crucible to thoroughly moisten the silica; 1-10 drops of 1:1 sulfuric acid (the greater amount when titania is high); and then 15 ml of hydrofluoric acid. Place the crucible on an aluminum hot plate set with a surface temperature slightly over 100°C (too low to cause boiling or spatter) until all silica and excess hydrofluoric acid have been removed. Add a few drops of water, pack the crucible 1/3 full of ashless paper pulp, add several drops of ammonium hydroxide, and burn off the paper, preferably by putting the crucible in a cold muffle furnace and slowly raising the temperature to 450°C over several hours. Finally ignite strongly, cool in the desiccator, and weigh.

6. The loss in weight during the hydrofluoric-sulfuric-acid treatment is counted as silica, but it does not represent all the silica in the sample. Despite the double dehydration with hydrochloric acid, a little always remains in solution. This is usually (but not always) found almost entirely in the ammonia precipitate, from which it will be recovered. With rocks, it is quite permissible to make an empirical correction for this unrecovered silica, since it invariably amounts to about 0.10 to 0.20 percent. Whether or not a silica recovery from the ammonia group is worthwhile depends on the nature of the sample and the purpose of the analysis. Such a recovery is less meaningful when porcelain casseroles are used in the silica dehydration. In mineral analysis, especially when the exact percentage of silica and alumina is critical, as it may be in crystal structure work, silica recoveries should always be made from the ammonia group. The same is true in rock analysis when the sample involved is to be used as a standard. The residue remaining after hydrofluoric acid treatment of the silica will be left in the crucible and weighed with the ammonia group. The total weight of R_2O_3 will then be obtained using the empty crucible weight obtained immmediately after the fusion. It will be assumed that insufficient platinum was introduced from the platinum dish to cause difficulty. This will be true, generally, for simple rocks which do not contain large amounts of Fe. Fortunately, interfering elements in the silica determination are few. The chief ones are fluorine, tungsten, molybdenum, and boron. All but the first need seldom be considered in rock analysis.

The Ammonia Group (R_2O_3)

1. Prepare double filters by folding 11 cm Whatman No. 41 paper or S and S black ribbon paper (see comment 6) inside 11 cm S and S No. 589 white ribbon paper. Wash the filters with a little 2 percent NH_4Cl solution whose pH has been adjusted to 6.4.	1. See Systematic Analysis of Silicates by Lee C. Peck, Geological Survey Bulletin 1170, pp 26-30, for a general discussion of the ammonia group. Pre-preparation of the filter papers results in saturated fibers; filtration will be faster. A 2 percent solution NH_4Cl may be prepared from 65 ml of the 15 percent solution diluted to 500 ml. The pH is checked with the nitrazine paper and adjusted with concentrated ammonia.
2. In the filtrate from the silica, put a small square of hardened filter paper under the end of the stirring rod to prevent bumping, so that a slow steady boil can be maintained. Heat the filtrate, which should have a volume of not more than 200 ml, and usually contains 5-20 ml of hydrochloric acid. Boil for 5-10 minutes or until there is no detectable odor of HCl. Add a few drops of bromine water if high iron samples have been evaporated in platinum; continue to boil until a drop of methyl red retains its color in solution for at least 3-5 minutes.	2. Boiling removes dissolved oxygen, CO_2, and reduces manganese entirely to the divalent state. Bromine water insures the complete reoxidation of iron because the reaction: $Pt + 4Fe^{+3} + 6Cl^- \rightarrow PtCl_6^{-2} + 4Fe^{+2}$ occurs in platinum. Manganese will be oxidized and precipitated upon neutralization if all the bromine is not driven off.
3. Cool somewhat. Add 50 ml of 15 percent solution of NH_4Cl.	3. The addition of NH_4Cl is governed by the amount of Mg expected. To prevent magnesium precipitation with the ammonia group, samples containing 50 percent MgO (dunite, periodotite) require at least 15 grams of ammonium chloride.

4. Add pure ammonia slowly with gentle stirring until iron just begins to precipitate; avoid an excess. Heat the solution almost to boiling and then add ammonia dropwise with stirring until a piece of nitrazine paper dropped into the solution assumes a green color, indicating a pH close to 6.0. Heat just to boiling (one roll over), check the pH by adding another small square of nitrazine paper, adjust with ammonia if necessary, finally bringing pH as close to 6.4 as possible. Stir, wash down the sides of the beaker with a little water, let stand for not more than a minute, and filter.	4. Pure ammonia is prepared by passing ammonia gas from a cylinder into freshly boiled water cooled in ice and protected from atmospheric CO_2. pH must be kept below 6.5 to prevent precipitation of Mn. Nitrazine paper is used because it floats and is easier to observe than the brown precipitate-laden filtrate.
5. During the filtration, keep the papers from running dry until the whole of the solution has been added. Then let the filter drain and wash with hot 2 percent ammonium chloride solution. The gelatinous mass should be broken up by a stream of liquid from the wash bottle beginning at the top of the cone and spiraling downward. The upper edges of the paper should be washed with particular care. About 100-150 ml of wash solution are normally used. There is no need to transfer all the precipitate, but the beaker should be rinsed three or four times.	5. Ammonium chloride rather than ammonium nitrate is used because a combination of nitrate and chloride makes complete reduction of Mn almost impossible. Also, nitrate prevents the complete precipitation of Mn by persulfate later in the scheme.
6. When washing is complete, and the filter has drained thoroughly, remove the soft inner paper containing the precipitate, being careful not to disturb the outer paper or break the column of liquid in the funnel stem. Spread the paper with the precipitate on the inner wall of the precipitation beaker. Wash the precipitate from the paper with a jet of water, fold the paper and reserve it.	6. In some instances (see comment 8), a third ammonia precipitate may be contemplated, in which case the paper is returned to the filter funnel. For three precipitations it is advantageous to use S and S black ribbon paper instead of Whatman No. 41 for greater wet strength.

7.	Wash down the sides of the beaker with 1:20 hydrochloric acid, add 5-10 ml of concentrated acid (more if manganese minerals are involved), and heat to boiling. Add water to a minimum of 150-200 ml; boil until methyl red is no longer decolorized in the boiling solution, and the odor of chlorine is no longer detected.	7.	The solution is boiled to remove oxidizing substances.
8.	Precipitate with ammonia as before except that the reserved No. 41 or the black ribbon paper should be torn up and macerated in the solution after the preliminary neutralization of most of the acid and before precipitation is complete. Heat just to boiling, wash down the sides of the beaker with water, make a final check of pH with nitrazine paper, and filter through the reserved paper.	8.	Normally, any further addition of ammonium chloride is not necessary in this second precipitation. A third precipitation of the ammonia group may be necessary with manganese minerals, samples containing large amounts of iron or aluminum, or when chromium, phosphate, arsenate, and some other unusual constituents are present. With ordinary rocks, two careful precipitations will leave only negligible amounts of calcium, magnesium, manganese and the alkalies in the precipitate.
9.	Wash the pulp remaining in the beaker by decantation, using hot 2 percent ammonium chloride solution, squeezing the pulp with the stirring rod, and pouring the washings through the filter. Repeat this two or three times, then transfer everything to the filter with the aid of a policeman. Wash very carefully, particularly around the top edges of the paper. Churn up the precipitate and pulp with the hot wash liquid.		
10.	Add to the beaker a little 1 + 1 HCl; wash down the sides with hot 5 percent HCl; digest for a few moments; add a drop of methyl red and ammonia to neutralize. Heat again. Add paper pulp and filter through a separate small paper into the filtrate.	10.	It is impossible to scrub the beaker free of metal hydroxides; therefore the hot HCl step is necessary.

11. Finally wash the precipitate thoroughly to remove most of the NH_4Cl, making the last wash with 10-20 ml of cold water. Do not disturb the precipitate. Drain the filter, break the column of liquid in the stem, and wash off the end of the funnel. Cover the funnel containing the precipitate with a piece of filter paper, through which moisture may escape, until it is dry enough to be conveniently handled. Place on the steam bath the covered filtrate which contains calcium, magnesium and manganese.

12. Transfer the bulky precipitate to the crucible containing the residue from the silica determination as follows: Tear an 11 cm filter paper in half, and roll it into a cone, with the point at the center of the torn edge. Put the point of the cone in the crucible, making a sort of funnel. Turn the paper containing the precipitate upside down, and fit the top edge into the improvised paper funnel. Using another piece of filter paper, press the mass down into the crucible. With pair of blunt Pt-tipped tweezers, pack the whole into the crucible, pressing it away from the sides as much as possible. Also add the small paper from step 10.

13. Place the crucible and precipitate in a cold muffle furnace, raise the temperature slowly to about 425°C, and leave at this temperature for several hours, preferably overnight. Then increase temperature to about 900°C., cool in a desiccator, and weigh. Repeat the ignition to constant weight, increasing temperature to as high as 1100°C if aluminum is high. Samples containing much iron need not be heated to as high a temperature; they should be held at about 750°C for some time before a final weighing.

11. The final wash with H_2O removes the slight possibility that iron may be lost as a volatile chloride during the ignition of the oxides.

The filtrate is heated because sometimes more R_2O_3 precipitate appears in the form of a cloudiness or a brown precipitate. The solution must be filtered again and the precipitate added to the bulky R_2O_3. A white granular precipitate is usually $CaCO_3$.

12. The residue in the crucible consists of TiO_2, Fe_2O_3, Al_2O_3 and P_2O_5. However, if present in the original sample, columbium, tantalum, probably tungsten, unattacked chromite and tourmaline, barium sulfate, and zirconium phosphate may also be present.

With the use of a paper cone, even the bulkiest of ammonia precipitates can be contained in a 25 ml crucible without difficulty. During ignition, it will collect into a single fluffy mass in the middle of the crucible, with none of the oxides adhering to the sides.

Recovery of SiO_2 from the Ammonia Group and Removal of Platinum Due to Crucible Attack.

1. Add to the mixed oxides 20 times their weight of potassium pyrosulfate, and heat covered over a small flame, gradually increasing temperature after 20-30 minutes until the crucible bottom is a dull red. Complete solution could take an hour and may be tested by letting the uncovered crucible cool in a good light; mass becomes transparent with cooling.	1. Fumes of SO_3 perform the function of dissolving the oxides. Therefore, too strong heating will result in loss of most of the excess SO_3 before attack is complete. The platinum crucible will be attacked by $K_2S_2O_7$; therefore the platinum lost in the Na_2CO_3 and $K_2S_2O_7$ fusions must be removed from the dissolved R_2O_3 group and weighed. See step 6.
2. When fusion is complete, cool on a porcelain plate, and add to the crucible about 10 ml of water. Heat on steam bath for 5 minutes and then transfer contents to a 250 ml beaker, scrubbing and washing the crucible thoroughly. Ignite and weigh the crucible for use in calculating the ammonia group.	
3. Add 10 ml 1:1 sulfuric acid and digest on steam bath until all solubles have dissolved. Transfer beaker to hot plate, uncover, and evaporate to fumes. Continue heating until a watch glass placed over the beaker no longer shows condensate.	
4. Cool, add 50 ml H_2O, stir, heat immediately on the steam bath to dissolve all but the fleecy SiO_2. Add paper pulp and filter immediately through a small fine paper into a 250 ml beaker. Transfer everything to the paper and wash carefully with 1:99 H_2SO_4 to a volume of about 80 ml.	

5.	Burn off the paper in the ignited and weighed crucible (step 2), ignite at 1000°C, cool, and weigh. Add to the residue a drop of sulfuric acid and several ml of hydrofluoric acid; evaporate to dryness. Ignite the crucible again, cool, and reweigh. Fuse the residue with one gram potassium pyrosulfate, dissolve melt in a few ml H_2O, take up with 10 percent sulfuric acid, and add to the main solution in the beaker. Wipe off the crucible, ignite, and weigh.	5.	The contents of the crucible consist of silicon and iron. After evaporation with H_2SO_4 and HF, only the Fe remains and is added to the dissolved ammonia group. Total SiO_2 should include the SiO_2 just recovered.
6.	Evaporate the solution to 50 ml. Cool, and add to the cold solution just 3 grams of granulated zinc. Allow to stand until reaction subsides. Then evaporate to a small volume on the steam bath, dilute to about 50 ml, let stand overnight, and filter off the precipitated platinum. Wash with 1 percent sulfuric acid, ignite at 900°C, cool, and weigh.	6.	Washing must be exceptionally thorough, as removal of the soluble metal sulfates is quite difficult.
7.	Add a few ml HF to the crucible, evaporate on a hot plate, ignite at 900°-1000°C, cool, and weigh.	7.	Often granulated zinc contains traces of SiO_2 which must be driven off to obtain the exact weight of platinum removed from the crucible.
8.	Analyze the ammonia group for TiO_2, Fe_2O_3, P_2O_5, and Al_2O_3 on a separate fusion. The $LiBO_2$-HNO_3 solution for K and Na is used to determine Fe_2O_3, TiO_2, and P_2O_5 colorimetrically. Al_2O_3 may be determined by difference or colorimetrically from the same solution.	8.	See separate procedures for the alkalies, TiO_2, Fe_2O_3, P_2O_5 and Al_2O_3.

Manganese

1. Evaporate in a liter beaker the combined filtrates from the ammonia group precipitate to about 250-275 ml. Heat to boiling after transfer to a 400 ml beaker (preferably the same one in which the ammonia precipitation was conducted). Put a piece of hardened filter paper under the end of the stirring rod.	1. Most or all of the manganese will normally be found in the filtrate from the ammonia group. However, both the Ca and Mg precipitate must be tested for Mn. Beryllium and the rare earth elements, if any, are not precipitated at pH 6.4. They are found in the ammonia group filtrate.
2. To the boiling solution, add dropwise a freshly prepared 25 percent solution of ammonium persulfate and, alternately with it, drops of 1:1 ammonium hydroxide, in such a way that the pH of the solution remains between 5 and 7. Acidity of the solution may be measured by adding a small square of nitrazine paper from time to time, and observing the color it assumes on touching the solution.	2. Ammonium persulfate decomposes in the boiling solution with the production of free acid. Addition of ammonia is necessary because manganese is reduced in hydrochloric acid solution at lower pH. About a half hour is required for complete precipitation of manganese. It appears that trivalent manganese is first formed, and this disproportionates into Mn (II) and Mn (IV), the latter precipitating as $MnO(OH)_2$. If this is indeed the mechanism of the reaction, the fact that it proceeds slowly, and requires alternate additions of persulfate and ammonia for the best results, is explained.
3. Collect the manganese precipitate on an 11 cm No. 40 paper and the filtrate in an 800 ml beaker. Wash the precipitate with 1 percent ammonium sulfate. Using water and leaving the paper in the funnel, wash the precipitate from the paper into the precipitation beaker. Dissolve it by adding a minimum of 3 percent sulfurous acid.	
4. Pour the solution through the filter, collecting it in a 150 ml beaker. Wash the paper thoroughly with water. Make sure the paper is free from sulfite. Reserve the paper to catch the second precipitation.	4. The filter paper is reused because traces of Mn and $BaSO_4$ may be retained on the paper.

5. Put a piece of hardened paper under the stirring rod and bring the solution to a slow steady boil. When most of the sulfite is gone, add several drops of 25 percent ammonium persulfate, and boil until precipitation is substantially complete. Then slowly add ammonia until the acid is neutralized. Continue boiling, with small alternate additions of persulfate and ammonia, until precipitation is complete. Adjust pH to 6-7, and filter. Wash with ammonium sulfate.	
6. Evaporate the combined filtrates in an 800 ml beaker to a volume of approximately 400 ml. Set aside for Ca and Mg.	6. The evaporation eliminates excess NH_3.
7. Return the Mn precipitate in its filter to the precipitation beaker. Place the beaker in a well-ventilated muffle furnace. Slowly bring the temperature to about 500° to ash paper. Cool the beaker and treat the residue with 20 ml 1 percent H_2SO_4 and several drops of H_2O_2. Allow to stand for several hours at room temperature to permit manganese to dissolve. Any residue is filtered through No. 42 paper and discarded unless barium has been requested. In that event, proceed with steps 8, 9, and 10--total sulfur procedure.	7. A residue, after manganese is dissolved, may contain barium sulfate (a white crystalline precipitate), platinum, and numerous oxides including silica. Rare earths, if present, will dissolve with the manganese. In the residue, additional traces of many elements have been found spectrographically including bismuth, antimony, lead, beryllium, molybdenum, iron, aluminum, copper and nickel. None of these adversely affect the total analysis with the exception of beryllium and the rare earths. The only element which may be almost completely recovered from the ignited Mn precipitate is barium.
8. Evaporate the filtrate on steam bath to near dryness, then heat on hot plate till fumes of SO_3 appear.	8. Peroxide must be removed as it interferes in the color reaction.
9. Add 50 ml H_2O, 10 ml HNO_3 and 10 ml 1 percent periodic acid. Cover and heat on steam bath overnight to develop the pink permanganate color.	9. $2\ Mn^{++} + 5\ IO_4^- + 3H_2O \rightarrow 2MnO_4^- + 5\ IO_3^- + 6H^+$.
10. Cool and transfer solution to 100 ml volumetric flasks. Dilute to mark and mix well. Prepare a series of standard Mn solutions from either a 1000 ppm solution or from a 20 ppm solution with predeveloped color.	10. If a colorless 1000 ppm solution is used, color must be developed with nitric acid and periodate.
11. Read the absorbance of samples and standards at 545 nm. Prepare a calibration curve by the least squares method. Report unknowns as percent MnO.	

Calcium

1. Place a small piece of hardened filter paper under the end of the stirring rod and bring the combined filtrates from step 6 to boiling. Add 40 ml of 10 percent (w/v) oxalic acid. Continue boiling while adding NH_4OH slowly until the solution is alkaline to methyl orange. Interrupt the addition of ammonia while a precipitate is forming. Finally, add 2-3 ml of ammonia in excess, check that the pH is 6 or slightly higher, and set aside to cool overnight.	1. A new batch of oxalic acid should stand a day and then be filtered before use. Boiling insures the precipitation of calcium oxalate as the monohydrate, a coarse, filterable precipitate which will not creep during filtration and washing. The filtrate from the ammonia precipitate may be treated in several ways. Manganese may be removed with sulfide or persulfate (described previously). Nickel may be removed with dimethylglyoxime. Residual rare earths or beryllium may be removed by addition of more ammonia. Carbonate may be used to separate combined calcium, strontium, and barium. Removal of ammonium salts may be desirable in certain cases. Ideally, however, only calcium, remnants of manganese, and magnesium are present. In this procedure, the calcium is separated as oxalate and is determined as carbonate. The magnesium and manganese are precipitated together as ammonium phosphates, ignited to pyrophosphates, and weighed. Manganese in the calcium and magnesium precipitates is determined colorimetrically; residual calcium is removed from the magnesium and manganese pyrophosphates, and determined.
2. Using No. 42 paper and a 1000 ml beaker, filter and wash the precipitate with 0.1 percent ammonium oxalate solution.	
3. Rinse the precipitate from the filter back into the precipitation beaker with water and dissolve in hot 5 percent HCl.	3. Calcium oxalate does not dissolve readily in dilute hydrochloric acid. Therefore, it is necessary to sluice it from the paper and wash the paper three or four times with 1:1 hydrochloric acid to be sure all the calcium is dissolved.

4. Place a 600 ml beaker under the funnel and filter the hydrochloric acid solution through the paper to remove traces of platinum, silica, etc. Wash very thoroughly with dilute hydrochloric acid.	
5. Wash filter paper free of acid using methyl orange indicator.	
6. Through the washed filter paper and to the filtrate containing magnesium, add 7 grams $(NH_4)_2HPO_4$ dissolved in a small volume of water.	6. Dibasic ammonium phosphate often contains debris.
7. Dilute the HCl solution so that it contains no more than 0.2 g of CaO per 100 ml. Carefully precipitate from boiling solution as before, but add only about 1 ml of 10 percent oxalic acid when precipitation is substantially complete. Digest hot (on steam bath) for an hour. Set aside to cool.	7. In the first precipitation, the large excess of oxalate and ammonium salts helps to prevent the post-precipitation of magnesium, but enough of the latter may still remain to cause error if the second precipitation is permitted to digest for more than a few hours. If but little magnesium is present, the recovery of calcium may be rendered more complete by longer standing.
8. After four hours, filter, save the filtrate, and transfer all the precipitate to the paper. Wash the paper and precipitate as before. Transfer to a small platinum, gold, or porcelain crucible which has been heated to 475°C, cooled, and weighed. Place uncovered in a cold muffle furnace and bring up to 475-500°C gradually; then hold at that temperature for several hours (overnight). Weigh as $CaCO_3$.	8. If the paper is burned off too fast, it is likely that some carbon may remain unburned at 500°C. A furnace which permits free access of air during ignition is needed. Do not exceed 500°C, however; above approximately 550°C, $CaCO_3$ loses CO_2. Ignition to CaO is not recommended. CaO avidly takes up H_2O and, moreover, slowly reacts with CO_2 in the atmosphere.
9. Inspect the $CaCO_3$. If it is pure white, no Mn is present. If it is off-white or brown, manganese has co-precipitated with calcium, and a correction should be made. See Recovery of Manganese from Calcium.	

Manganese Recovery From Calcium

1. Dissolve the $CaCO_3$ in dilute HNO_3; make the solution 10 percent in HNO_3. Add one drop H_2O_2 to dissolve Mn (fizzes violently).	
2. Evaporate the solution to near dryness on the steam bath to destroy H_2O_2. Cool. Wash down sides of beaker with water.	2. Peroxide must be removed as it interferes with the color reaction.
3. Add approx. 0.1 g periodic acid or potassium periodate, and heat near the boiling point (steam bath), for several hours or longer if necessary. Cool.	3. Permanganate color development may even take several days.
4. Make to volume. Compare with standard solutions by reading absorbance at 545 nm.	4. The size of the volumetric flask is chosen on the basis of the intensity of color which develops.
5. Handle the data in the usual linear regression manner. Adjust $CaCO_3$ weight by assuming the Mn was weighed as Mn_2O_3. Calculate the recovered Mn as MnO.	

Calculations:

$\frac{mg}{ml}$ MnO (calculated from the equation) x vol. in ml
= mg MnO

$$\frac{Mn_2O_3}{2MnO} = \frac{156.87}{70.94} = 2.225 = \text{gravimetric factor}$$

mg MnO x 2.225 = wt. of Mn_2O_3

wt. of $CaCO_3$ - wt. of Mn_2O_3 = corrected wt. of $CaCO_3$.

Magnesium

1. Combine the filtrates from the two calcium oxalate precipitates and make the solution 10 percent in concentrated ammonia. Allow to stand at least 48 hours (a week if Mg is low) with frequent stirring, striking the walls of the beaker to initiate precipitation.	1. See Quantitative Chemical Analysis by Kolthoff, Sandell, Meehan, Bruckenstein, pp. 631-641, for a discussion of magnesium.
2. Filter through a large (11 or 12.5 cm) blue ribbon paper and wash superficially with 5 percent ammonia.	2. Large filter paper is used because of the great volume of solution.
3. Leaving the paper in the funnel, dissolve the precipitate in hot 5 percent hydrochloric acid. Rinse the liter beaker, pour the rinsings through the filter paper, and collect filtrate in a 250-ml beaker.	
4. Add 1.5 ml of 15 percent ammonium chloride solution for every 10 mg of MgO expected. Dilute to 50-100 ml or to 200 ml if more than about 20 percent MgO is present. Add a little methyl red indicator and then ammonia solution dropwise just to the neutral color of the indicator.	4. Avoid striking the walls of the beaker with the stirring rod during this precipitation. If precipitation begins while adding ammonia, pause to let large crystals form. A cloudy fine precipitate is to be avoided.
5. Add ammonia slowly with stirring until precipitation is substantially complete.	5. As little as 1.50 percent MgO appears. With high magnesium, most can be precipitated without making the solution strongly alkaline.
6. Make the solution 10 percent in concentrated ammonia; stir frequently for an hour or more; then add 1 ml of 25 percent diammonium phosphate solution.	
7. Stir occasionally, each time washing down the sides of the beaker with 5 percent ammonia solution, and leaving a layer of dilute ammonia on top of the solution. This hastens precipitation. Let stand overnight.	

8. Before filtering, stir the solution several times; filter through a small Whatman No. 42 paper and wash thoroughly with 5 percent ammonia solution, transferring all the precipitate to the paper. Transfer paper and precipitate to a weighed porcelain or platinum crucible and burn off the paper at as low a temperature as possible--250°C. Then ignite at 1100°C until all carbon is removed. Weigh as $Mg_2P_2O_7$ + $Mn_2P_2O_7$.

9. After weight is constant, break up the pyrophosphate in the crucible with a small, sharp spatula to be sure that no carbonaceous matter remains. If any black material is seen, the ignition should be repeated, at a higher temperature if necessary. Magnesium pyrophosphate retains its weight up to about 1200°C. At higher temperatures, loss of P_2O_5 is possible.

8. Often there is some difficulty in removing all carbon during the ignition. Commonly a small part of the pyrophosphate remains stubbornly black, even after many hours ignition, unless the conditions of the ignition are closely controlled. Presumably, carbon becomes graphitized and is protected from the air by the precipitate. This difficulty can be avoided by first charring and then burning off the paper at as low a temperature as possible with a good air supply. The use of a well-ventilated muffle is essential, particularly if platinum crucibles are used.

9. A careful investigation of the conditions necessary to insure the weighing of stoichiometric $Mg_2P_2O_7$ is discussed by Hillebrand, Lundell, Bright, and Hoffman, Applied Inorganic Analysis, pp. 636-639.

Calcium Recovery From Magnesium

1. To the crucible containing the ignited and weighed pyrophosphates, add a little water and 1 ml of 1:1 sulfuric acid. Warm gently and transfer the contents of the crucible to a 150 ml beaker, using a policeman if necessary.	
2. Heat on the steam bath until solution is complete, adding more sulfuric acid if necessary, up to a total of 5 ml (of 1:1) for 1 g of magnesium pyrophosphate. Finally add water to make the solution 5 percent in H_2SO_4. The total volume will usually be 25 ml.	2. No more than 2.5 ml of 1+1 H_2SO_4 may be added if <1 g magnesium pyrophosphate is present.
3. Cool and add as nearly as possible three times the volume of absolute ethanol. Allow to stand with occasional stirring for several hours (overnight) for complete precipitation of calcium sulfate.	3. EtOH must be between 75 percent and 80 percent by volume.
4. Filter through a 11 cm Whatman No. 44 paper and wash superficially with 80 percent (v/v) alcohol. The beaker and filter should be kept covered as much as possible during this filtration to prevent evaporation of alcohol, with resultant solution of the calcium sulfate.	4. The alcohol washing solution should be made fresh with each usage. One hundred sixty ml of ethanol is added to 40 ml water in a graduate.
5. Drain the filter and beaker thoroughly, uncover them, and let stand until all alcohol has evaporated.	
6. Dissolve the $CaSO_4$ by adding 5 percent HCl to the precipitation beaker and pouring the acid through the filter paper using just enough solution to dissolve the precipitate.	6. Catch the dissolved $CaSO_4$ in a 150 ml beaker.
7. Add 1 ml of 10 percent oxalic acid, heat to boiling, and add an excess of NH_4OH.	
8. Digest hot, cool, let stand for four hours, filter through No. 42 paper, wash with 0.1 percent ammonium oxalate, transfer to a crucible, burn off paper, and ignite to $CaCO_3$ at 475°C.	8. The filtrate from this step is discarded.

9. Cool and weigh. Subtract the weight directly from that of the magnesium pyrophosphate; add the weight to corrected wt. of $CaCO_3$ calculated in step 5, Manganese Recovery From Calcium. Convert total $CaCO_3$ to CaO by multiplying by 0.5602, the gravimetric factor $\frac{CaO}{CaCO_3}$.

9. The weight of $Ca_3(PO_4)_2$, the form as it existed in the magnesium precipitate, equivalent to $CaCO_3$ recovered is almost equal.

Conversion Factors:

$$CaCO_3 \underset{1.0330}{\overset{0.9680}{\rightleftarrows}} Ca_3(PO_4)_2$$

Manganese Recovery From Magnesium

1. Evaporate the filtrate from the calcium sulfate on the steam bath, then heat to incipient fumes on a hot plate. Test for dryness by placing a watch glass over the beaker for a few moments. There should be no condensate on the watch glass.	1. Cl^- traces are removed.
2. Dilute with a little water and filter into a 150-ml beaker.	
3. Make the solution 10 percent in nitric acid, add about 0.1 gram of periodic acid or potassium periodate, and heat on the steam bath until oxidation of manganese is complete, i.e. until the pink color develops. Cool.	3. Color development has been known to take a weekend.
4. Dilute to exactly 100 ml or more if Mn is high. Prepare a series of dilute standards from a stock solution of $KMnO_4$. Measure the absorbance of standards and unknowns at 545 nm. Treat the data by the method of least squares.	
5. Calculate the manganese found to $Mn_2P_2O_7$ and subtract its weight from the weight of the $Mg_2P_2O_7$ calculated in step 9, Calcium Recovery From Magnesium. Convert total $Mg_2P_2O_7$ to MgO by multiplying by 0.362, the gravimetric factor $\frac{2MgO}{Mg_2P_2O_7}$.	5. If manganese was not determined previously, the sum of the manganese found in the calcium carbonate and that found in the magnesium pyrophosphate should come very close to the total manganese in the sample. If it does not, it is almost certain to have been retained in the ammonia precipitate; this occurs when much phosphate is present in the sample, when iron is very high, when the ammonia group is precipitated at too high a pH, and/or under certain other conditions.

Example of Calculations:

mg/ml MnO (calculated from equation) x vol. in ml = mg MnO.

$$\frac{Mn_2P_2O_7}{2\ MnO} = \frac{283.82}{141.87} = 2.0005 = \text{gravimetric factor}$$

mg MnO x 2.0005 = mg $Mn_2P_2O_7$

Because the Mn in the $Mg_2P_2O_7$ precipitate was ignited to $Mn_2P_2O_7$, the weight thereof is subtracted directly from the weight of the $Mg_2P_2O_7$.

The results of the Main Portion analysis are reported in the following order:

SiO_2, Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O, K_2O, H_2O^+, H_2O^-, TiO_2, P_2O_5, MnO.

Percentages should be reported to two decimal places.

Compiled by M. Cremer

CLASSICAL ANALYSIS
INTERFERENCES IN SILICA DETERMINATION

(From an unpublished procedure by C. O. Ingamells)

The most common interference is fluorine, which in a silica determination causes low results, due to the volatilization of fluorosilicic acid. The problem may be handled in several ways:

1. A large excess of aluminum chloride may be added to the HCl used to dissolve the sodium carbonate fusion. Aluminum complexes fluorine and prevents the loss of silica by volatilization.
2. Boric acid may be added before the HCl addition to drive off BF_3.
3. The sample may be heated with perchloric and boric acid. Boric acid is volatilized from perchloric acid, which removes the fluorine as BF_3.

Procedure For Number 1	Comments
1. Determine moisture, omit roasting, and fuse 0.6 to 1.0 gram of sample in the usual way.	
2. Leach with H_2O in a platinum dish in the usual manner.	
3. When melt has completely disintegrated, acidify by adding 50 ml of 10 percent (w/v) $AlCl_3 \cdot 6H_2O$ in 1:3 HCl.	
4. Dehydrate silica as usual; however, make a third dehydration to insure complete capture of silica.	4. The large amount of aluminum decreases the efficiency of the dehydration process. Normal recovery of silica from the ammonia group is not feasible.
5. Discard the filtrate unless the sample contains rare earths when the filtrate may be used to determine them.	
6. The analysis is continued on another portion of the sample by removing the silica in the usual manner, i.e. without the addition of $AlCl_3 \cdot 6H_2O$.	6. The silica is discarded and the analysis is continued by precipitating the ammonia group from the filtrate.

Procedure For Number 2

The following procedure is applied to tourmaline, a boron-bearing mineral, which also contains appreciable fluorine.

1.	Fuse the sample in the usual way with Na_2CO_3, leach in platinum with H_2O, and add 10 ml of 5 percent boric acid before HCl addition.	1.	Boron accompanies silica and is volatilized by the HF treatment causing high results for silicon. Therefore, it must be removed by evaporation. See comments 2 and 3.
2.	Evaporate uncovered to dryness on the steam bath.	2.	$BF_3\uparrow$
3.	Cool. Add alternately 2 to 3 ml of concentrated HCl and 2 to 3 ml of methanol, cooling the dish before each addition and evaporating to dryness afterwards, always with the dish uncovered. Do not overheat. Loss by splattering can occur.	3.	$B(OCH_3)_3\uparrow$
4.	After several treatments with alcohol and acid, continue with the silica determination and ammonia group precipitation as usual.		
5.	Ignite the ammonia precipitate in silica or Vycor crucibles, separate from the R_2O_3 residue left from the silica determination.	5.	Boron removal is often not complete, so the ammonia group must be examined for traces.
6.	When the ammonia group precipitate reaches constant weight, mix the oxides thoroughly with a platinum rod or spatula.		
7.	Weigh approximately 10 mg of the precipitate in a gold crucible. Add a pellet of sodium hydroxide and heat just to fusion.		
8.	Cool. Add H_2O and leach.		
9.	Evaporate to 0.1 ml and proceed with the determination of boron by the curcumin method of Hayes and Metcalfe.	9.	<u>Analyst</u>, Vol. 88, pp. 471-476, (June 1963).

Procedure For Number 3

The following procedure is applied to fluorite where fluorine is part of the chemical formula.

1. Prepare a boric-perchloric acid solution saturated with H_3BO_3 by adding an excess of H_3BO_3 to a mixture of 25 ml $HClO_4$ and 70 ml H_2O and heating with stirring to 80°C.

2. Weigh 0.500 g of the sample into a 400-ml pyrex beaker and add 15 ml of the hot acid.

3. On a hot plate, digest uncovered below the boiling point until most of the H_2O is expelled.

4. Gradually increase the heat until the perchloric acid fumes. Continue heating for five minutes after strong fumes are evolved.

5. Cool, wash down the sides of the beaker with H_2O, and repeat the evaporation and fuming.

6. Dilute the residue with 50-75 ml of H_2O, heat to boiling, and filter.

7. Wash with 1:20 HCl and H_2O as usual; transfer all insolubles to the filter.

8. Transfer the filter to a platinum crucible, add 2 drops concentrated H_2SO_4 (to decompose any CaF_2); pack half full of ashless paper pulp, add several drops of ammonia, and burn off the paper at as low a temperature as possible.

9. Ignite strongly, cool, weigh and reheat, if necessary, to constant weight.

10. Determine SiO_2 as usual; i.e. by volatilization with HF.

11. Continue the analysis with the precipitation of the ammonia group, etc. as usual. However, if the group is large, it should be examined for boron contamination--see steps 6-9, Procedure for No. 2--Classical Analysis-Interferences in Silica Determination.

Compiled by M. Cremer

CLASSICAL ANALYSIS

INCOMPLETE ATTACK OF SAMPLE

(From an unpublished procedure by C. O. Ingamells)

Some minerals which resist Na_2O_3 attack are chromite, kyanite, magnetite, ilmenite, tourmaline, beryl, zircon, and sillimanite. A gritty residue during fusion-leaching with H_2O or acid indicates that the analysis should be started again with a more finely ground sample and/or a longer or hotter fusion or a stronger oxidant. Sodium peroxide in platinum may be used.

Procedure	Comments
1. Tare on a platform balance the crucible containing the sample; quickly add 3-4 grams of Na_2O_2 and mix with a platinum or silica rod.	1. Na_2O_2 is hygroscopic and a powerful oxidizing flux to be used when Na_2CO_3 is ineffective. Also, ore minerals of metals such as Cu, Pb, Ag, As, etc. might alloy with the platinum during a Na_2CO_3 fusion.
2. Weigh 1 gram Na_2CO_3 on weighing paper and cleanse the rod by rotating it in the carbonate.	
3. Sprinkle the Na_2CO_3 over the contents of the crucible. Cover and heat in a 500°C muffle for one hour.	3. Temperature must be carefully controlled because above 500°C Na_2O_2 attacks platinum rapidly--even more severely if much Mn or Cr are present. The fusion can never be done by flame.
4. Cool, place the crucible in the dish or casserole which is to be used for the silica determination, cover, and add 50 ml of H_2O.	
5. Warm cautiously if solution is slow.	5. Once solution begins, it proceeds rapidly with boiling and evolution of oxygen.
6. When the solution becomes quiescent, acidify with HCl to limit the attack on the vessel by the hot alkali, proceeding as in a Na_2CO_3 fusion--see Classical Analysis-Main Portion.	

Compiled by M. Cremer

TOTAL SULFUR

Sulfur is determined gravimetrically as $BaSO_4$. Most of the sulfur occurs as sulfide in the form of pyrite (FeS_2) or pyrrhotite (Fe_7S_8). Sulfur-bearing silicates are more rare; small amounts of sulfates may be present in the form of barite, celestite, gypsum, alunite. Elemental sulfur or organic compounds containing sulfur are unusual. So that all sulfur-bearing portions are attacked and oxidized, the sample is fused in an alkali flux. The melt is leached, filtered, and the filtrate is rendered acidic. Barium chloride is added to the filtrate; the resulting precipitate is ignited and weighed as $BaSO_4$. Cr can be determined colorimetrically on the filtrate before acidification. The residue from the filtrate contains barium, nickel, zirconium, hafnium, and the rare earths.

Procedure	Comments
1. Weigh 0.5 g sample in a Zr crucible. Mix well with 3.5 g Na_2O_2 and sprinkle a small amount of Na_2CO_3 over the mixture.	1. The sample should not be ground too fine or there is danger of oxidizing sulfide to sulfur dioxide. Na_2CO_3 slows down the rapid oxidation process. Zr crucibles are used because Na_2O_2 attack on Pt is severe at temperatures greater then 450-500°C. In addition, if much sulfur is present, platinous sulfide forms on the crucible.
2. With a Tirrill burner, begin to gently heat the crucible. Then gradually heat the crucible to bottom redness while swirling now and then to check for undecomposed lumps. The inner core of the flame should form a button on the bottom of the crucible.	2. Na_2O_2 sends forth small hot grains if heated too quickly. If much organic material is present, the mixture may even catch fire with attendant loss of sample. In addition, care must be taken to exclude flame gases. The combustion products of gas contain oxides of sulfur avidly taken up by alkaline fluxes and solutions.

3. When the fusion is complete, cool the crucible somewhat and place it in a 150 ml beaker covered with a watch glass. Cautiously add, a little at a time, approx. 25 ml H_2O. Place on steam bath until reaction is quiet. Remove the crucible, rinsing it well with H_2O and policing the interior. The volume in the beaker is approx. less than 50 ml.	3. Alternatively, H_2O may be added to the covered crucible while it is hot. The reaction is usually so swift that the crucible must be placed quickly in cold H_2O to quench the reaction and avoid overflow.
4. Return beaker to steam bath where it should remain for approximately an hour. Remove from steam bath and let stand overnight. Next morning, filter through no. 42 filter paper within which is folded 41H paper. Use a 400 ml beaker. Wash well with 1 percent NaOH. If other elements are to be determined, quantitatively transfer the residue to the paper and set it aside. Add a few drops of methyl red to the filtrate.	4. The filtrate contains sulfur and chromium. The residue contains barium, zirconium, and nickel.
5. Calculate the amount of 1+1 HCl necessary to render the filtrate just acid and provide a 1-2 percent excess. Add the entire amount of acid at once. The total volume in the beaker will be about 200 ml. Place a small piece of 41H filter paper under the stirring rod in the beaker.	5. If HCl is added dropwise, Si will precipitate in great quantities rendering the filtration of $BaSO_4$ impossible. Filter paper beneath the stirring rod prevents bumping as the solution boils.
6. Begin heating the filtrate with a small Tirrill burner flame. When it is boiling gently, add dropwise through the center hole in the watchglass approx. 15 ml of 10 percent $BaCl_2$ solution. Pause in the addition of the $BaCl_2$ while precipitation is occurring. If the methyl red decomposes, add more to be sure solution is acid.	6. Do not boil too long. Si will precipitate.
7. Digest on the steam bath. Remove and let stand overnight. Stir occasionally.	

8. Filter through no. 42 paper contained within a 41H paper. Wash thoroughly with cold H_2O, using very small portions, as $BaSO_4$ is sparingly soluble in H_2O.	8. $BaSO_4$ is soluble to the extent of 2.4 mg/liter at 20°C. It is soluble to the extent of 6 mg/100 ml in 3 percent HCl.
9. Burn off paper and ignite to constant weight at about 700°C in a weighed Pt crucible.	9. The precipitate is easily reduced to sulfide by carbon formed in filter paper charring. Therefore, paper should be charred very slowly at low temperature with free access of air.
10. To the crucible containing the $BaSO_4$, add a drop of H_2SO_4 plus a few drops of HF. Evaporate to dryness on a hot plate. Reignite and reweigh.	10. Some silica may have separated with the $BaSO_4$. After HF treatment, one ignition of the $BaSO_4$ is sufficient. For a discussion on the methods of reporting sulfur, see reference 1, pp. 235-236.

Compiled by M. Cremer

CONVERSION FACTORS

$$\mathrm{BaSO_4} \underset{7.2807}{\overset{0.1374}{\rightleftarrows}} \mathrm{S} \qquad \mathrm{BaSO_4} \underset{3.6438}{\overset{0.2744}{\rightleftarrows}} \mathrm{SO_2} \qquad \mathrm{BaSO_4} \underset{2.9156}{\overset{0.3430}{\rightleftarrows}} \mathrm{SO_3} \qquad \mathrm{BaSO_4} \underset{2.4299}{\overset{0.4115}{\rightleftarrows}} \mathrm{SO_4}$$

$$\mathrm{SO_2} \underset{1.9981}{\overset{0.5005}{\rightleftarrows}} \mathrm{S} \qquad \mathrm{SO_3} \underset{2.4971}{\overset{0.4004}{\rightleftarrows}} \mathrm{S} \qquad \mathrm{SO_4} \underset{2.9959}{\overset{.3338}{\rightleftarrows}} \mathrm{S}$$

REFERENCES

Kolthoff, I. M., Sandell, E. B., Meehan, E. J., Bruckenstein, Stanley, 1969, Quantitative Chemical Analysis, 4th ed.: New York, Macmillan Co., p. 602-617.

Maxwell, John A., 1968, Rock and Mineral Analysis: New York, Interscience Publishers, p. 234-243.

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SULFUR TRIOXIDE

(Quoted verbatim from Systematic Analysis of Silicates, p. 82, Geological Survey Bulletin 1170, by Lee C. Peck)

Water is added to a 1.0000-gram portion of the sample. The water is boiled, and after hydrochloric acid is added, boiling is continued for an additional 15 minutes. The solution is filtered, and the filtrate is neutralized with ammonium hydroxide and then reacidified with hydrochloric acid. Sulfate ions are precipitated by the addition of barium chloride. The solution is filtered, and the paper containing the precipitate is burned off in a weighed platinum crucible. The crucible and its contents are ignited and weighed.

Sulfide sulfur is determined by difference after separate determinations for total sulfur and for sulfur trioxide.

Procedure

1. Transfer a 1.0000-gram portion of the sample into a 250-ml Erlenmeyer flask. Place a spray trap (fig. 6) in the neck of the flask. Add 80 ml of water, and bring it to a gentle boil over a Tirrill burner. Boil the water for 1 minute; then add 20 ml of 1-to-1 hydrochloric acid through the funnel, slowly enough so that the solution does not stop boiling. Continue boiling gently for 15 minutes.

2. Wash off the inside and outside of the funnel trap, and remove it from the flask. Add 0.25 gram of paper pulp, and filter the solution through a 9-cm fine-porosity paper into a 400-ml beaker. Use a short stirring rod, which should be kept in the funnel, to make the transfer. Wash down the inside of the flask three times with 1-to-19 hydrochloric acid, and transfer the washes to the filter. Finally, wash the paper five times with the same solution, and discard it.

3. Add five drops of brom cresol purple indicator to the filtrate. Neutralize the solution with ammonium hydroxide. Add 1-to-1 hydrochloric acid by drops until the indicator turns yellow; then add 2 ml more. Dilute the solution to 200 ml.

4. Add 5 ml of a 10-percent barium chloride solution. Heat the solution for 2 hours on the water bath, and stir it occasionally during this period; then let it stand overnight at room temperature.

5. Filter the solution through a 7-cm fine-porosity paper into a clean 150-ml beaker. Discard each 50-ml portion of the filtrate as it collects, provided it is clear; but if a portion of the filtrate is turbid, refilter it. Transfer the precipitate to the paper using water, and wash the paper five times with water.

6. Burn off the paper in a weighed 25-ml platinum crucible ... Heat the crucible with the cover partially open over a Tirrill burner at a dull-red heat for 15 minutes. Cool the crucible in a desiccator for 30 minutes, and weigh it. (Alternatively, burn off paper in a muffle furnace and ignite to constant weight at ~700°C.)

7. Calculations:

   Weight $BaSO_4 \times 34.3$ = percent SO_3.

Discussion

Pyrite and some related minerals do not dissolve in hydrochloric acid. Other sulfide minerals dissolve and liberate hydrogen sulfide, in some reactions, precipitate sulfur. The added water is first boiled to expel air. The hydrochloric acid is added, and hydrogen sulfide, if liberated, is expelled by boiling, without danger of being oxidized to the sulfate. Pyrite and any precipitated sulfur are filtered from the solution.

Without considerable knowledge of the mineralogy of the sample, a reliable analysis for sulfur trioxide cannot be made. Sulfur trioxide is generally present as one or more of the calcium sulfate minerals, which dissolve readily in hydrochloric acid, and if they are the only sulfate minerals present, the analysis is accurate.

Barite and scapolite do not dissolve in hydrochloric acid, and if routine procedures for the determination of sulfur are followed, their sulfur will be reported as sulfide sulfur. The sulfate in celestite is probably incompletely dissolved.

The sulfate contained in alunite and some related sulfate minerals is only partly extracted by boiling the sample with hydrochloric acid. Alunitic sulfate is almost completely extracted by boiling the sample with 5-percent sodium hydroxide, but this treatment does not dissolve calcium sulfate. If a mixture of alunite and calcium sulfate minerals are present, the sample must be boiled first with sodium hydroxide and then with hydrochloric acid in order to recover all of the sulfate. If the analysis is made by boiling with sodium hydroxide, the solution is filtered, and the filtrate is acidified with hydrochloric acid; the sulfate is precipitated as barium sulfate. Only a few analyses have been made by using this procedure, and how sulfide minerals are affected by treatment with sodium hydroxide is not known.

Although procedures can be planned by which the various sulfates and sulfides can be determined separately, it is rarely advisable to attempt such separations. The total amount of sulfur is generally so small that the errors in the individual determinations would be larger than the sulfur content of a particular mineral. If small amounts of sulfur are present, it is best to determine and report total sulfur and to allow the petrographer to estimate its mineralogical distribution.

FIGURE 6.—Spray trap. This trap, made from a transfer funnel, prevents loss by spraying if a solution must be boiled.

TOTAL WATER - PENFIELD METHOD

Total water - hygroscopic or surface and occluded or chemically bound - is determined gravimetrically. The powdered sample is mixed with a $PbO:PbCrO_4:CuO$ flux and heated in a Meker burner flame. The condensed water is collected in the cool portion of the Penfield tube and weighed.

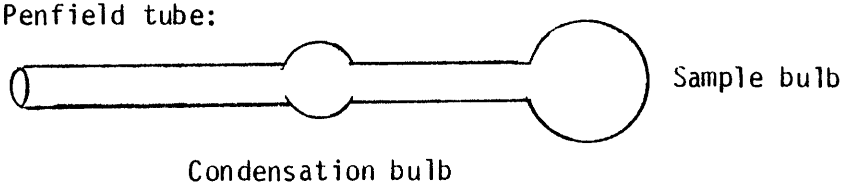
Reagents (all chemicals-reagent grade):

Prepare a $10+1+1:PbO:PbCrO_4:CuO$ flux by mixing intimately and igniting (uncovered) at 400°C for thirty minutes. Store in a desiccator.

Procedure

1. In a small porcelain crucible, weigh 0.50 g of the sample and 2.0 g flux. Mix thoroughly.

   Penfield tube:



2. To a clean dry Penfield tube, introduce the sample and flux mixture with the aid of a long-stem funnel. The funnel tip should extend slightly (6-7 mm) into the sample bulb. Tap the funnel gently to insure a quantitative transfer.

3. Remove funnel; then close the tube with a special capillary stopper. Care must be taken so that none of the powder adheres to the tube walls.

4. Around the condensation bulb, wrap a damp cloth and carefully place the tube horizontally into the special ice bath. The sample bulb should be as far away from the ice bath as possible. Place a Meker burner directly under the sample bulb.

Comments

1. The ratio of flux to sample should be approximately 4:1. The flux serves to decompose the sample and retain the volatiles. Since the flux is slightly hygroscopic, it should be ignited every two to three days or when a blank exceeds 0.0009 g in weight. The blank (consisting of flux only) must be determined at regular intervals, and after each ignition period.

2. The Penfield tubes should be cleaned and stored in an oven at 105°C. Allow the tubes to cool for thirty minutes prior to weighing and loading the sample. A maximum of four determinations can be performed simultaneously.

4. If a supply of dry ice is readily available, it may be substituted for conventional ice. In that event, omit the damp cloth.

5. Starting with the sample bulb well above the flame (~10 inches to 1 ft.), heat gently for five minutes. Next, lower the ice bath and tube approximately one-quarter the height between the sample bulb and flame. Continue this process at five minute intervals until the sample bulb is just above the blue flame. Throughout the heating, lightly tap the tube with the tips of a pair of tongs while rotating the tube slowly to spread the sample evenly around the sample bulb. Replenish ice to keep the condensation bulb covered at all times. The total heating process should be approximately thirty minutes.	5. Heating the sample too rapidly causes the surface water, if it is too high, to escape from the tube.
6. When the process is complete, the sample and flux should be in a molten state. Using a gas-oxygen hand torch, heat the sample bulb while rotating the tube slowly. Draw off the sample bulb with a pair of tongs and heat the remaining end of the tube to insure proper sealing. Turn off the Meker burner. Do not dispose of the sample bulb.	6. The hand torch may be used anytime after fifteen minutes into the heating process to promote melting of the powder. When the torch is used, be sure to rotate the tube to keep the red-hot glass from sagging and to avoid rupturing the sample bulb.
7. Allow the tube to cool momentarily in the ice bath. Take the tube from the bath, remove the cloth and capillary stopper. Immediately place a special dry glass rod into the tube and replace the stopper. Always handle the tube so the stoppered end points up.	7. The glass rod should fit the tube snugly but permit the replacement of the stopper. The rod serves to displace CO_2 from the tube.
8. Dry the tube with a clean cloth, place it near the balance, and allow the tube to equilibrate for thirty minutes. Handling the tube with chamois, remove the stopper and weigh.	
9. Place the unstoppered tube, containing the rod, in the oven at $105^{0} \pm 5^{0}C$ for a period of at least two hours.	9. Overnight is convenient.
10. Remove the tube and rod from the oven, place near the balance, allow to equilibrate for thirty minutes, and weigh.	10. The difference in the two weights of the tube (weight in step no. 8 - weight in step no. 10) represents (theoretically) the total water content of the sample (less the H_2O in the blank). Percent total H_2O = $\frac{\text{(difference in weight - blank } H_2O \text{ weight)(100 percent)}}{\text{Weight of Sample}}$
11. The sample bulb drawn from the tube should be cracked open and checked for complete decomposition of the sample (i.e. glassy surface, no lumps...).	

REFERENCES

1. Hillebrand, W. F., Lundell, G.E.F., Bright, M. S., and Hoffman, 1953, Applied Inorganic Analysis, 2nd ed.: New York, John Wiley and Sons, Inc., p. 814-835.

2. Kolthoff, I. M., Sandell, E. B., Meehan, E. J., and Bruckenstein, Stanley, 1969, Quantitative Chemical Analysis, 4th ed.: Toronto, Collier-Macmillan Canada, Ltd., p. 573-579.

ACID DECOMPOSITION FOR ATOMIC ABSORPTION ANALYSIS

An acid breakup of rocks and minerals is preferred when traces are to be analyzed by atomic absorption. The total dissolved solids are decreased with concomitant diminution of various interferences. The sample is heated initially in equal volumes of HNO_3, $HClO_4$, and H/F. The solution is evaporated to dryness, taken up in equal volumes of HNO_3 and $HClO_4$, and again evaporated to dryness. The dried solids are heated in 1+1 HCl and made to volume. Preliminary runs of the requested elements on the atomic absorption are made to determine if dilution is necessary.

Procedure	Comments
1. Weigh 1.00 g each premixed samples and transfer to teflon crucibles. At the same time, prepare 3 or 4 rock standards covering a span of concentrations.	1. The sample size may be reduced with a corresponding decrease in volume depending upon the number of elemental analyses requested. Rock standards are used to check the calibration curve, or might even be needed to construct the curve.
2. Add in the following order: 10 ml HNO_3 10 ml $HClO_4$ 10 ml HF At the same time, prepare an acid blank.	2. HNO_3 must always be added first to oxidize any organic material present. $HClO_4$ can be highly explosive in the presence of organic material.
3. Cover and place on hot plate with surface temperature set at ~100°C. Let stand overnight.	
4. Cool. Remove covers and wash down sides and covers with a minimum of water. Return the crucibles to the hot plate. Gradually increase the surface temperature to ~225°C.	4. Teflon has rather poor dimensional stability even at room temperature. As temperature is raised, its resistance to deformation decreases rapidly. At temperatures above 285°C, it may begin to decompose.
5. Continue heating until crucibles cease fuming. Cool and wash down the sides of the crucibles with a minimum of water. Add 10 ml HNO_3 and 10 ml $HClO_4$.	5. Heating to fume cessation results in the removal of Si as gaseous SiF_4.
6. Return crucibles to hot plate. Take to the cessation of fumes again.	
7. Cool. Wash down the sides of the crucibles with H_2O. Add 10 ml of 1+1 HCl to each. Transfer the contents quantitatively to pyrex beakers and place on steam bath to complete dissolution. Check for residues.	7. Often the residue, when filtered, washed, and weighed is negligible; e.g. $\leq$ a few milligrams; i.e. a few parts in a thousand.

8. Cool and make to 100 ml in volumetric flasks.

9. Run the solutions on the atomic absorption to determine what dilutions are required.

10. Prepare the necessary dilutions endeavoring to have the concentrations provide between 30 and 50 percent absorption. Also prepare standards from "pure" solutions matching the density to the samples by using the appropriate acids.

11. After determining absorbance on the AA, prepare a calibration curve by the least squares method using the "pure" standards data. Compute the concentration in ppm (microgram per gram) in the rock standard solutions. Check the concentrations against the recommended values.

12. If the concentrations of rock standards do not agree within ±10 percent with the recommended values, prepare a calibration curve using the weight-corrected rock standards data.

13. If the rock standard data do not produce a reasonably straight line nor an acceptable curve, the method of standard additions must be used.

9. An effort should be made to reduce the number of dilutions for the different elements to as few as possible.

10. The uptake rate on the AA is determined by the viscosity of the solutions. A difference > 1 percent between standards and samples leads to error.

12. If agreement is not within ±10 percent, there are matrix interferences. "Pure" solution standards cannot be used for that element.

13. See <u>Analytical Methods For Flame Spectroscopy</u>, Varian Techtron, pp. 14-15.

Micro pipettes should be used. Volume changes are negligible then, and the method seems to produce better results. Varian recommends this.

Compiled by M. Cremer

DETERMINATION OF BORON IN SILICATES

(From Determination of Boron in Silicates after Ion Exchange Separation, Henry Kramer, Anal. Chem., v. 27, no. 1, January 1955, p. 144-145.

The sample is fused with sodium carbonate, acidified with hydrochloric acid, filtered, neutralized with sodium hydroxide, and the solution eluted from an ion exchange column. Boron is determined titrimetrically in the presence of mannitol using a pH meter to indicate the end point.

Reagents (all chemicals-reagent grade):

Mannitol, neutral, boron-free.

Amberlite IR 120(H) - exchange capacity of the dry resin approximately equal to 5 mg per gram.

Sodium hydroxide, 20 percent w/v carbonate free.

Sodium hydroxide, 0.05 N standardized with $KH(IO_3)_2$, and methyl red as indicator.

Procedure	Comments
1. Fill with water a borosilicate chromatograph tube 20 x 400 mm. Add slowly a slurry of the resin to a column length of 10 inches. The column should be free of air spaces.	1. The resin may be regenerated after use by transferring accumulated resin from a number of determinations to a large glass tube and washing with 1+9 HCl until the rinses give a negative test for adsorbed ions. HCl is removed by washing with water.
2. Before using, wash the column with 100 ml of 1+9 hydrochloric acid and follow with 50 ml portions of water until effluent gives a negative test for chlorides.	2. A silver nitrate crystal may be used to test for chlorides.

3. Weigh sufficient sample not to exceed 1 gram but which contains no more than 20 mg B_2O_3 into a platinum crucible. Also weigh a portion of NBS 93, a borosilicate glass, as a control.

4. Add six times the sample weight of anhydrous sodium carbonate and mix intimately. Cover the crucible, fuse, cool, and place the crucible in a 150-ml beaker containing 20 ml of water.

5. Cover the beaker with a watch glass and add concentrated HCl down the side of the beaker until there is an excess of 1 ml over the theoretical amount needed to decompose the carbonate.

6. When the reaction has ceased, dissolve any carbonate adhering to the crucible or cover with dilute HCl. Remove any adhering material with a rubber policeman and rinse into the beaker with a stream of H_2O.

7. Filter the mixture through 9 cm Whatman 41H filter paper and wash with hot H_2O to a volume of about 50 ml.

8. Neutralize the above solution until a precipitate just begins to form. Add concentrated HCl dropwise until the precipitate just dissolves.

3. NBS 93 contains 12.76 percent B_2O_3. Therefore, where x = sample weight, solve the following equation for x. (0 .1276)(x mg) = 20 mg B_2O_3; x = 156.7 mg, a weight not to be exceeded. 0.05 N NaOH is to be used subsequently in the titration. Since 1 ml 0.05 N NaOH = 1.741 mg B_2O_3, and a microburet calibrated to 0.02 ml (10 ml capacity) is to be used, it is wise to calculate sample weight more exactly as follows:

$$x = \text{sample wt.}$$

$$\frac{(.1276)(x\ \text{mg})}{1.741\ \text{mg/ml}} = 9.5\ \text{ml}$$

$$x = 129.6\ \text{mg NBS93}$$

or less depending upon the volume of NaOH desired. This calculation insures that the microburet need not be filled twice. Also, this amount of sample meets the requirement of <20 mg B_2O_3.

5. $Na_2CO_3 + 2HCl \rightleftharpoons 2NaCl + H_2CO_3 \rightleftharpoons H_2O + CO_2$.

9.	Pour the solution through the ion exchange column into a 400-ml beaker and follow with four 50-ml portions of water, adding more wash water when there is 0.5 inch of supernatant solution in the resin. Adjust the flow rate so that the total elapsed time for the solution and 4 washings is 15 minutes or 16.7 ml per minute.	9.	At the conclusion of the final washing, the effluent should be only slightly acid to pH paper.
10.	Add 2 or 3 drops of methyl red indicator to the solution and make alkaline with 20 percent sodium hydroxide and then barely acid with concentrated HCl.		
11.	Cover the beaker with a watch glass and boil for 3 to 5 minutes to remove CO_2. Cool to room temperature in a water bath.		
12.	Place the pH meter electrodes and a stirrer into the beaker and adjust the pH of the solution to 7.0 with 0.05 N NaOH.	12.	The readout should be steady at 7.0.
13.	Add 40 grams of mannitol and, with a microburet, titrate rapidly with 0.05 N NaOH until the pH approaches 7 and then slowly near the end point, thus allowing for any slight lag in meter response.	13.	Mannitol with its multiple hydroxyl groups converts the weak boric acid into a relatively strong acid, thus permitting a more accurate titration.
14.	When the reading remains steady at 7.0 for at least 10 seconds, record the volume of standard base used.		
15.	Prepare and determine the reagent blank. Subtract the blank titration from the sample titration. Calculate percent B_2O_3 using 1 ml 0.05 N NaOH = 1.741 mg B_2O_3.	15.	The blank is usually <0.10 ml of 0.05 N NaOH.

REFERENCES

Hillebrand, W. F., Lundell, G.E.F., Bright, H. A., Hoffmann, J. I., 1953, Applied Inorganic Analysis, 2nd edition, John Wiley & Sons, Inc., New York.

Kolthoff, I. M., Sandell, E. B., Meehan, E. J., Bruckenstein, Stanley, 1969, Quantitative Chemical Analysis, 4th edition, The Macmillan Company, Collier-Macmillan Canada, Ltd., Toronto, Ontario, p. 783, 787-788.

CARBONATE CARBON IN SILICATES, CARBONATES, AND PHOSPHATES

Carbonate carbon, also referred to as acid soluble or inorganic carbon, is determined using a CO_2 coulometer. The coulometer cell is filled with a partially aqueous medium containing monoethanolamine and a colorimetric indicator. When the liberated acid-soluble CO_2 is passed through the solution, CO_2 is quantitatively absorbed and, upon reaction with monoethanolamine, is converted to a strong titratable acid, causing the blue indicator color to fade. The coulometer electrically generates base to return the color to its original intensity. The coulometer displays units of µg CO_2. The accuracy is 0.1 percent for samples containing over 1 mg carbon. A more complete description and installation procedure can be found in manual[1].

Procedure

1. Freshly fill the pertinent tubes as follows:

   A. Fill air scrubber tube with approx. 12 ml of 45 percent KOH.

   B. Fill sample scrubber tube with approx. 3 ml of 1 percent $AgClO_4$ and 0.3 ml H_2O_2.

2. Cell Filling:

   A. Place approximately 70 ml of coulometer solution in the cell body (beaker). The entire light beam must pass through solution. Make sure sufficient solution is used so that the stirring vortex will not be in the light beam.

   B. Add stirring bar.

   C. Be sure cell cap is appropriately assembled (Figure II reproduced from the instruction manual and attached).

   D. Place a few crystals of KI inside the anode compartment.

   E. Place cell cap on the cell body and add anode solution to the anode compartment so that when the silver electrode is in place, the anode solution level will be the same as the solution level in the cell body, and the electrodes are tilted back toward the labeling on the cell body.

Comments

1. The KOH removes CO_2 from the carrier air. If excessive foaming occurs, add a few drops of H_2O or replace the KOH.

F. Place cell in coulometer cell holder with the electrodes to the back.

G. Be sure cell current switch is off. Turn on coulometer.

H. The anode compartment frit and gas inlet tube should be positioned so that they are just above the stirrer but in back of the light beam. This may be checked by rotating the cell until maximum Percent T is observed. The Pt electrode should project out and just in the light beam for the highest sensitivity.

I. The Percent T knob should be adjusted to give about 100 percent T (this setting is not highly critical, but must not be changed during analysis). If the Percent T meter is not steady, check to see that the gas stream is bubbling away from the light beam.

J. Plug in electrodes noting polarity (cathode-black, anode-red).

3. Fill acid dispenser bottle with 2N $HClO_4$; check delivery syringe for 2 ml.

4. Turn on cell current, heater (a 2:00 o'clock setting), and air pump (set rotometer at 100 cc/min).

5. Allow the coulometer to titrate to the end point and to stabilize. Check for leaks if stabilization does not occur.

6. Reset counter.

7. Weigh a sample in a porcelain boat or other carbonate free sample carrier and drop entire carrier into sample tube. Normally sample size is selected so that 1 to 3 mg of carbonate carbon is evolved (i.e., 100 mg SCo-1 gives 2500 µg CO_2 or 2.50 percent acid-soluble CO_2).

3. Perchloric acid is non-oxidizing in dilute solution. Care should be exercised to avoid concentrating the acid.

5. Typically this takes 2-5 minutes and depends upon the amount of CO_2 absorbed by the system and the solutions, as the equipment was being prepared for operation.

7. At high current (100 ma), 750 micrograms/minute of carbon is titrated.

8. Reconnect the sample tube and allow system to purge the CO_2 which entered while the sample tube was disconnected.

9. Reset counter.

10. Press plunger to dispense about 2 ml acid.

11. Rotate tube onto heater.

12. Allow sample to purge until coulometer gives a relatively stable reading. Record reading and dispose of sample and acid.

13. Reset coulometer and run next sample (step No. 7).

14. Calculation:

$$\frac{(\text{Micrograms C} - \text{blank}) \times 100}{\text{Micrograms sample}} = \text{Percent carbonate carbon } (CO_2)$$

15. Cell Changing and Clean-up:

The cell solutions should be changed daily even when use is light. Cell solutions should be replaced if over 100 mg of carbon have been titrated.

A. Turn off cell current and coulometer power.

B. Unplug electrodes and remove cell from holder.

C. Dispose of coulometer solution and rise cell body.

D. Remove silver electrode and rinse with water.

E. Rinse outside of anode compartment, gas inlet tube, and Pt electrode with water.

F. Rinse out the anode compartment with acetone. Use test tube brush to remove KI and deposits on top of the glass frit if necessary.

14. Normally the blank value is negligible (4μg CO_2 in 2500 μg), but should be recorded for low-level work.

15. The valve on the flow meter should be closed (flow turned off) before the pump is turned off. This will eliminate the possibility of KOH being forced back into the pump.

G. Pull acetone through frit with aspirator or other vacuum source. If acetone does not flow through the frit rapidly, the frit should be more thoroughly cleaned or replaced. Anode deposits can be removed with a saturated KI solution.

H. If a deposit is evident on the platinum electrode, this should be dissolved in 1:1 HNO_3. Prevent deposits by not leaving the cell assembly standing unused overnight or for extended periods when it is filled.

I. Dry all components.

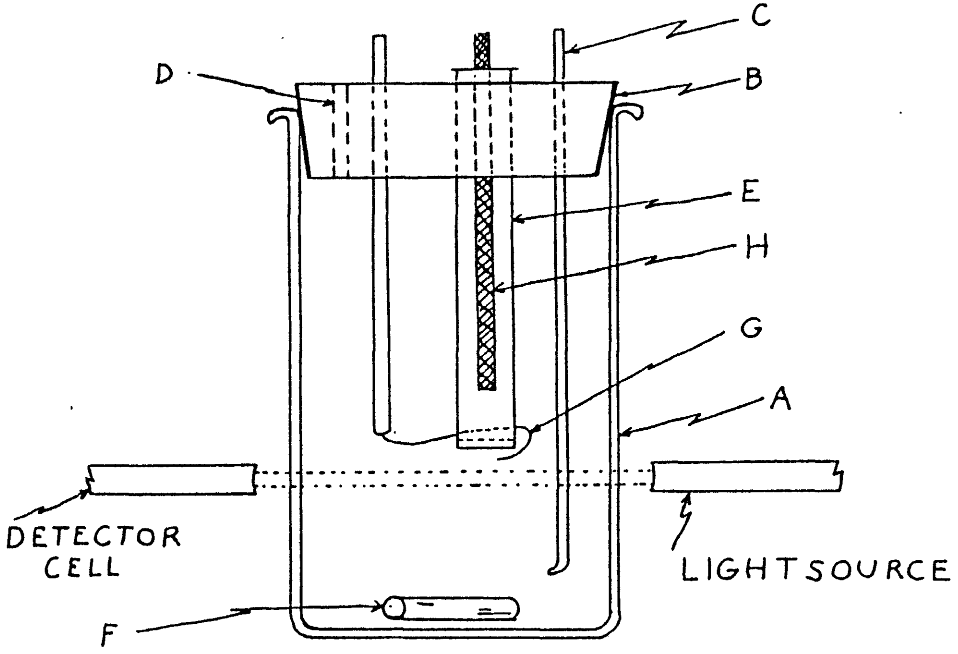
16. When analysis is complete:

A. Drain air scrubber, rinse with H_2O, then 1+1 HCl, then finally with H_2O again.

B. Drain sample scrubber, rinse with H_2O, then warm using water bath with NH_4OH in scrubber (to clean frit), and finally rinse with H_2O again.

Compiled by P. Klock

FIGURE II
COULOMETER CELL



a. Cell body
b. Cell cap
c. Gas inlet
d. Gas outlet
e. Anode compartment
f. Stirrer
g. Platinum electrode (cathode)
h. Silver electrode (anode)
i. Light path

REFERENCES

1. Coulometrics Incorporated Instruction Manual, P.O. Box 544, Wheat Ridge, Colorado 80033.

TOTAL CARBON CONTENT OF GEOLOGIC MATERIALS

A Leco WR-12 with an induction furnace is used in a combustimetric determination of total carbon in rocks$_1$. A thermal conductivity cell is the sensing device, with two instrument ranges of 0.005 percent - 0.20 percent C and 0.01 percent - 5.0 percent C. Up to 1.0 gram of powdered sample (<100 mesh) may be used, depending on the amount of carbon.

Approximately 20-25 samples can be analyzed in 4 hours. A detailed discussion of equipment may be found in References 2 and 3.

1. Prepare premixed -100 mesh sample so the weight corresponds to the expected percentage of carbon in the sample (use Table 1).
2. Quantitatively load the weighed sample into a 'Leco' crucible and cover with a labeled watch glass. To minimize contamination, handle 'Leco' crucible with tongs.
3. Perform an electronic checkout of the instrument.

   A. Check to see that Power On light is on. It must have been on for 4 hours.

   B. Close the positive-locking tray of the induction furnace.

   C. Turn on oxygen tank. Set Regulator at 35 psi. Depress O_2 switch. Set the oxygen flow at 1.5 on the rotometer. Oxygen must be on for 10 minutes.

   D. Turn the Carbon Range switch to 0.0050 to 0.200 percent C position and turn the Blank switch off (not glowing).

   E. Turn the function Select Switch to DVM Zero position and with a small screw driver adjust the DVM to read 0.000 ± 0.001. (The adjustment is accessible through a small hole in the DVM window.)

   F. Open the electronics drawer.

   G. Plug test lead into Text Jack socket of the DVM; plug the other end (red wire) into the +15 and the common test points. DVM should read between +0.1475 and +0.1525. If not, adjust R14 on the ± 15 VDC card.

   H. Plug test lead into -15 (Red wire) and common test point. DVM should read between -0.1475 and -0.1525. If not, adjust R13 located on the ± 15 volt card.

I. Depress the Stand-by switch. Plug test lead into Bridge test points. DVM should read between ± 0.0580 and ± 0.0620. If not, adjust the Bridge Curr. control located on the function adjust panel. If adjustment needed, wait 10 minutes for stabilization.

J. Remove test lead from test points and test plug from Test Jack. Close electronic drawer.

K. Depress Stand-by switch. Turn Function Select switch to Pre-amp Zero position. DVM should read between +0.006 and -0.006. If not, adjust P/A Bal control on the function adjust panel.

L. Depress the Stand-by switch. Turn the Function Select switch to the T/H Balance position. Observe DVM for at least one minute. It should read between +0.006 and -0.006. If not, set the T/H Bal control on the function adj. panel as set forth on p. 4-1, no. 7 of instruction manual.[2]

M. Depress the Stand-by switch. Turn the Function Select switch to the Integ Bal position. DVM should read between +0.006 and -0.006. If not, adjust Int-Bal control on function adjust panel until 0.000 is achieved.

N. Turn Function Select switch to Bridge position. DVM should read between +0.0020 and -0.0020. If not, adjust Bridge Bal control located on function adjust panel, If adjustment needed, wait 10 minutes for stabilization.

O. Depress Stand-by switch. Set Range switch to high range position. Turn Function Select switch to Operate position for approximately 30 seconds. Now turn Function Select switch to Integ Check position and note time. At end of one minute, note reading. DVM must not change more than ±0.001.

4. Depress Filament Voltage.
5. Rotate Function Select switch to Calibrate position.
6. After one minute, depress High Voltage.
7. Positive-locking tray of induction furnace should still be closed.
8. Check that combustion time is 70 seconds.
9. Sample weight compensator should read 1.000 grams.
10. Depress standby. Turn off Blank switch if it is on (off=not glowing).
11. Load into 'Leco' crucible one scoop of Cu accelerator and one scoop of Fe chips (Cu on bottom). Prepare several; these will be the blanks.
12. Place a blank on pedestal; close and lock positive-locking loading tray.

13. For low-scale operation (0.005-0.20 percent C), proceed directly to No. 31.

14. Carbon Range switch should be on 0.010 to 5.000 percent C position.

15. After approximately 30 sec, depress the green analyze switch.

16. After the carbon indicator turns white and the Analyze goes off, unload the hot crucible and place another blank on the pedestal; close and lock the positive-locking loading tray.

17. Record DVM when Carbon indicator turns green.

18. After both Carbon and Analyze are green, depress Analyze. Whole cycle repeats on the second blank.

19. Proceed with blanks until two in a row read approximately ≤0.007.

20. Next burn a 0.350 percent standard in the above manner. DVM should read ±1 percent of C value or ±0.002 percent C, whichever is greater. (Tolerance is on the ring standard bottle).

21. If reading is not within tolerance, run another as above. Note DVM reading.

22. If step 21 is not within tolerance, run another standard. When Carbon light turns green, unlock and adjust High Percent Carbon control until DVM is within tolerance.

23. Run one more standard to be sure DVM is repeated.

24. Now prepare and run a series of a blank plus standards in the Operate position. If all is well, proceed with unknowns, running the same series of standards at the end of the sample run. During each run, watch the plate current meter on the furnace. It should register >500 ma. Visually check each sample for complete combustion. If the meter never reaches 500 ma, weigh a smaller portion of the sample. Run 3 ring standards for a 4 pt. calibration curve. If standard values fall off, lance might be clogged.

25. At the end of the sequence (standards-samples-standards), depress Standby switch.

26. Turn off: High voltage, Filament voltage, Blank Switch, and Oxygen Tank.

27. After oxygen bleeds down, depress O_2 switch (light not glowing).

28. Turn Function selection switch to Pre-Amp zero. Set Range to high scale.

29. Dust trap and combustion tube area must be cleaned after 20-25 samples. Sample entrained Magnesium Perchlorate must be changed every 4 hours of sample usage. For general maintenance, see p. 7-1 of instruction manual[2].

30. Average the DVM results of the standard rings and perform a linear regression of the data. Standard rings are assumed to be 1 gram each.

31. Carbon Range switch should be on 0.0050-0.1000 percent C position.

32. After approximately 30 seconds, depress the green Analyze switch.

33. Carbon light will eventually turn white and Analyze light will turn green. When Analyze light turns off, remove crucible. Load another blank immediately.

34. When Carbon light turns green, record DVM. DVM should not be >0.0010 percent C.

35. Depress Blank switch (glows white).

36. Unlock the Blank Adjust Control (while Carbon is still green) and adjust to 0.000 on DVM.

37. Only when both Carbon and Analyze are green, depress Analyze. Second blank should read <0.0010. If it does not, adjust as in step 36.

38. Burn a ring standard of approximately 0.170 percent C. Reading must be within tolerance that is stated on the Ring standard bottle (+ or - 1 percent of C value). If not, adjust Low percent C control while carbon light is white.

39. Repeat 0.170 ring standard until acceptable DVM reading is obtained; adjust as necessary.

40. Repeat a blank and adjust Blank Adjust if necessary; if adjusted, the 0.170 ring must be burned and checked.

41. Check back and forth between low and high until no adjustment is necessary.

42. Proceed directly to No. 24 above and continue through No. 30.

Compiled by P. Klock

REFERENCES

1. Leco Corporation, St. Joseph, MI., WR-12 Instruction Manual.

2. Leco Corporation, St. Joseph, MI., Induction Furnace (model 763-200) Instruction Manual.

3. Tillman, John H. 1977, A Combustimetric Method for Determining the Total Carbon Content of Geologic Materials: Journal Research U.S. Geol. Survey, v. 5, no. 5, p. 583-587.

TABLE 1

General classification of some geologic materials for total carbon determination using the WR-12 carbon determinator

Material	Percent total C	Sample Wt.	Type Accelerator
Basalts, hornblende, diorite	0.005-0.010	0.75-1.0	Fe/Cu
Hornblendes, rhyolites, andesites, peridotite, granites, gneiss, diabase, basalt	.010-0.200	.50-1.0	Fe/Cu
Granodiorite, syenites, gabbro, granites	.100-0.500	.100-0.5	Fe/Cu
Sulfides, phyllites, syenites	.500-1.00	.100-0.5	Fe/Cu
Marine sediments, phosphate rocks, clays, tuff, limestones	>1.00	.100-0.5	Fe/Cu

POWDER DENSITY OF ROCKS

(Condensed from L. Shapiro, USGS Prof. Paper 650-B)

Finely crushed rock ($\leq$ 80 mesh) sinks or floats in a heavy liquid, if not agitated, as large aggregates of the constituent minerals rather than as discrete grains. The average density of the clumped, crushed material closely approximates that of the rock powder and may be determined by a simple sink-float technique. Small samples of powdered rock are centrifuged in heavy liquids in a sequence designed to bracket their densities within narrow limits. Only ~100 mg of sample is required to obtain a density determination within ±0.04 g/cm^3.[1,2].

Reagents (all chemicals-reagent grade):

Procedure

1. Freshly prepare eight heavy-liquid mixtures according to the proportions given in Table 1. Methylene iodide mixtures stored in amber bottles containing a small piece of copper wire minimizes light-induced decomposition and the alteration of the density by iodine release.

Table 1. Primary Mixtures

Liquid designation Bottles	Carbon Tetrachloride (Sp. gr. 1.59)	Bromoform (Sp. gr. 2.89)	Methylene Iodide (Sp. gr. 3.32)	Resultant Specific Gravity
A	25 ml.	22.5 ml.	---	2.20
B	20	29	---	2.36
C	14.3	35.7	---	2.52
D	8.3	43.7	---	2.68
E	2	50	---	2.84
F	---	33.3	11.5 ml.	3.00
G	---	20	33.3	3.16
H	---	---	50	3.32

2. To familiarize yourself with the method, run two or three standards (i.e. W-1 and Sierra Quartz; densities 3.00 and 2.64 respectively).

3. With a small spatula, transfer 40-50 mg of pre-mixed sample (<80 mesh) to two 10 ml conical centrifuge tubes. Usually each sample requires four (4) tubes.

4. Add 0.3 ml of liquid D to one of them. Do not agitate, but centrifuge for one minute and examine.

5. Classify the results as follows:

   a. The entire sample floats, or
   b. The entire sample sinks, or
   c. The sample splits to form one layer on top and one layer on bottom, or
   d. The sample is dispersed throughout the liquid in which case it has the same density as liquid D.

   When categorizing, ignore approximately 5 percent or less which may go in the direction opposite to that of the bulk of the sample.

6. If (a) occurs, add 0.3 ml liquid C to the second tube.
   If (b) occurs, add 0.3 ml liquid E instead to the second tube.
   If (c) occurs, add 0.3 ml liquid C to the second tube, and add 0.3 ml liquid E to a third tube to which has been added another portion of sample.

7. Centrifuge the tubes for one minute and categorize as in step 5.

8. If necessary, repeat with additional portions of sample until two adjoining liquids in table 1 are found in which the sample floats in one and sinks in the next.

9. When the two adjoining liquids are located, pour the contents of the two tubes back and forth to mix them producing a liquid of intermediate density, e.g. DE, whose specific gravity or density is 2.76. Centrifuge for one minute and categorize.

For example, decide upon the density as follows:

If The Sample:			
disperses or splits in:	floats in:	sinks in:	The resultant density is:
D	E	C	2.68
CD	D	C	2.60
		CD	2.64
	CD		2.56

If a sample forms two discrete layers in two adjoining primary mixtures, or if it sinks in the heaviest liquid, the density cannot be determined by this method.

REFERENCES

1. Shapiro, L., 1975, Rapid analysis of silicate, carbonate, and phosphate rocks, revised edition, USGS Bulletin 1401, p. 71.

2. Shapiro, L., 1969, Rapid determination of powder density of rocks by a sink-float technique, USGS Prof. Paper 650-B, p. 140-142.

Compiled by P. Klock and M. Cremer

DIGESTION METHOD FOR FLUORINE IN SILICATES

(Adapted from Determination of Fluoride in Silicate Rocks Without Separation of Aluminum Using a Specific Ion Electrode, Blanche L. Ingram, Anal. Chem., v. 42, no. 14, Dec. 1970)

Samples are sintered with sodium carbonate and zinc oxide, then digested overnight at steam-bath temperature. The residue is filtered off and is rejected. Nitric acid is added to the filtrate which is made to volume with water. Equal aliquots of filtrate and buffer are mixed, and the potential of the solution is measured with a specific ion electrode. Standards are prepared from a sodium fluoride solution and are matched to the samples with sodium carbonate and nitric acid. A plot of the log of the fluoride concentration as ordinate and EMF as abcissa produces a curve linear to approximately 0.4 ppm with a negative slope.

Reagents (all chemicals-reagent grade):

0.2 M sodium citrate - 0.2 M potassium nitrate solution. Dissolve 59 grams of sodium citrate dihydrate and 20 grams of potassium nitrate in water. Dilute to one liter.

Standard fluoride solution. Heat NaF in a platinum crucible at low red heat (640°C) for 1-2 hours. Cool, weigh 1.105 grams, dissolve in water, and dilute to 500 ml. Transfer to a polyethylene bottle for storage. 1 ml = 1000 μg fluoride.

Procedure	Comments
1. Weigh a 100 mg sample in a small platinum crucible. Mix with 0.5 g of anhydrous sodium carbonate and 0.1 g of zinc oxide.	1. Zinc oxide is added to provide a more grainy residue which traps more silicon.
2. Sinter at 900°C for 30 minutes. Place the cooled crucible in a glass beaker, add 30 ml of H_2O, cover the beaker, and digest on the steam bath overnight.	
3. Remove the crucible, catch rinses in beaker, break up any lumps, and allow the solution to cool to room temperature.	
4. Use Whatman No. 42 filter paper to filter the solution into a 100 ml volumetric flask. Wash the residue several times with small portions of 0.1 percent sodium carbonate solution. Reject the residue.	4. Chlorine is returned and found in the filtrate. It may be determined colorimetrically. See procedure for colorimetric chlorine.

5. Slowly add 1.5 ml 1 + 1 nitric acid to the solution, shaking vigorously to expel CO_2. Dilute to volume with water. Mix well.

6. Prepare a series of Standards as follows:

   To a 500 ml volumetric flask, add 2.50 grains sodium carbonate. Add water to dissolve. Carefully add to the flask 7.5 ml of 1 + 1 HNO_3. Dispel as much CO_2 as possible by shaking. Make to volume with H_2O. Mix. To a series of five 100-ml volumetric flasks, add 0.4 ml and 0.8 ml of 100 ppm F^- solution; 0.2 ml, 0.4 m., and 0.8 ml of 1000 ppm F^- solution respectively. Make to volume with the previously prepared $NaCO_3$ - HNO_3 solution.

7. Beginning with the lowest standard, i.e. 0.4 ppm, pipette 5.0 ml of the solution into a small plastic cap. Add 5.0 ml of the sodium citrate-potassium nitrate solution. Mix well. Immerse the electrodes in the solution. Continue slow mixing. Read and record the potential after 5 minutes. In the same manner, determine the potential of the remaining standards as well as that of the sample solutions.

8. Treating millivolts as the independent variable and the log of the concentrations as the dependent variable, prepare an equation by the method of least squares. Use the equation to calculate the concentrations of the knowns. Report in percent F^- to two decimal places.

5. It is extremely difficult to expel all the CO_2. Much care must be taken after dilution to volume. The volumetric stopper should be released periodically.

6. The procedure provides for a series of 0.4, 0.8, 2, 4, and 8 ppm F^- standards, to be used for a calibration curve. These standards can be used over a period of several weeks.

7. Potassium nitrate is used in the citrate solution to prevent electrode fatigue. The pH of the sample solutions after dilution with the citrate-nitrate solution is ~6.3. With this solution, aluminum does not interfere at the 28 percent Al_2O_3 level in solutions with 0.004 to 0.08 percent F^-. If more than 0.08 percent F^- is present, as much as 38 percent Al_2O_3 does not interfere.

8. A less rigorous method may be used by plotting the data on semi-log paper and reading the unknown concentrations from the graph.

Compiled by M. Cremer

REFERENCES

1. Ingram, B. L., 1970, Determination of fluoride in silicate rocks without separation of aluminum using a specific ion electrode: Anal. Chem., v. 42, no. 14, p. 1825-1827.

2. Orion Instruction Manual fluoride electrodes model 94-09, model 96-09, 1977.

STANDARD ADDITION METHOD FOR FLUORINE IN SILICATES

(Adapted from Determination of Fluorine in Silicates by Use of an Ion-selective Electrode Following Fusion with Lithium Metaborate, J. B. Bodkin, The Analyst, v. 102, no. 1215)

Samples are fused with lithium metaborate and dissolved in nitric acid. A complexing buffer is added, and the potential of the solution is determined with a pH meter with a absolute millivolt scale. A known volume of standard fluoride solution is added; the potential is again checked; and the concentration of fluoride in the sample is computed using the potential difference and the Nernst equation. Samples containing as much as 2.7 percent fluorine may be analyzed.

Reagents (all chemicals-reagent grade):

Lithium metaborate. Anhydrous $LiBO_2$.

Nitric acid, 2.56 percent v/v, arranged for delivery from a 50 ml teflon stopcock type automatic pipet.

Standard fluoride solution. Heat NaF in a platinum crucible at low red heat (640°C) for 1-2 hours. Cool, weigh 1.105 gram, dissolve in H_2O and dilute to 500 ml. Transfer to a polyethylene bottle for storage. 1 ml = 1,000 μg fluoride.

Complexing buffer solution. Add 18.2 g of DCTA (1,2-diaminocyclohexane-NNN'N'-tetraacetic acid), also known as DCYTA (1,2-cyclohexylenedinitrilo-tetracetic acid) to 1.5 liter of H_2O and then 40 percent m/v NaOH solution dropwise until the DCTA dissolves. Add 300 g sodium citrate dihydrate and 60 g NaCl, adjust the pH to 6.85 with HCl and dilute to 2 liter with H_2O. Arrange for delivery from a 50 ml teflon stopcock-type automatic pipet.

Procedure	Comments
1. Mix 80 mg sample with 320 mg $LiBO_2$. Transfer the mixture to a graphite crucible and fuse in a muffle furnace at 1050°C for 10 minutes.	1. At this temperature, some elements are not quantitatively retained; e.g., the alkalis, chlorine, and sulfur.
At the same time, fuse a blank and a standard rock in the same manner. Carry them, together with the sample, through the procedure.	
2. While the sample is fusing, add to a 4 1/2 oz (110 ml) polypropylene container (Falcon), a magnetic stirring bar and 50 ml of 2.56 percent HNO_3 with the automatic pipet.	2. The containers must be large enough to accomodate 100 ml plus the subsequent addition.

3. Begin stirring the solution magnetically as the fusion nears completion. Remove the crucible from the muffle, swirl it, and then pour the molten bead into the container.	3. Swirling the hot crucible insures more complete coalescence of the molten substance.
4. Cover the container and continue stirring until the sample is dissolved--usually about 15 minutes.	
5. When solution is complete, add 50 ml of buffer from the automatic pipet. Stir well. Cover. Set aside.	5. DCTA buffers the solution to a pH of approximately 5.5. At a pH below 5, hydrogen complexes fluoride as the undissociated acid HF and the ion HF_2^-. At a pH >7, hydroxide ion interferes when the level of hydroxide is greater than 1/10 the level of fluoride ion present. DCTA controls Al and Fe interference.
6. From the standard NaF solution prepare 10 and 100 ppm fluoride solutions.	6. These solutions are used to prepare a calibration curve as well as to add increments to the sample solutions.
7. Use the blank solution to prepare a calibration curve as follows: Add 0.2 ml of 10 ppm NaF solution to the blank, stir and immerse the electrodes in the stirring solution. When a constant potential reading is obtained (usually 5 minutes), record the millivolts. Continue in the same manner with the addition to the same solution of the following increments: 0.5 ml of 10 ppm 0.8 ml of 10 ppm 0.2 ml of 100 ppm 0.5 ml of 100 ppm 0.8 ml of 100 ppm 0.2 ml of 1000 ppm 0.5 ml of 1000 ppm 0.8 ml of 1000 ppm	7. The accumulated concentrations in µg/ml are 0.02, 0.07, 0.15, 0.34, 0.83, 1.60, 3.54, 8.34, and 15.93. The very small volume changes do not affect the significant figures shown.

8. Using semi-log paper, plot the concentration in ppm on the vertical or log axis and the mv readings on the horizontal axis. Draw a straight line from the highest concentration to 0.15 ppm. Determine the slope by subtracting millivolt readings a decade apart in concentration.

9. Immerse the electrodes in the sample solution, stirring as before. Record the millivolt reading after 5 minutes.

10. Use the foregoing reading with the graph to determine the apparent concentration in ppm of the unknown. Approximately double the apparent concentration; add that amount of standard fluoride to the solution, stir, and again record the potential after 5 minutes. This procedure should lead to a ΔE of ~15-30 mV.

8. The graph is to be used to read an approximate concentration of the unknown which must be at least doubled when the addition is made to the unknown.

   The theoretical slope varies with temperature, but between 20 and 25^{O}C, it is approximately 58 mv for a univalent electrode. The slope must be checked each time fluorine is determined. Only two solutions a decade apart in concentration are prepared and the potentials determined.

10. If an uncertainty of -0.5 mV in ΔE and -1.0 mV in slope is assumed, a minimum error results at a ΔE of approximately 15-30 mV.

11. Calculate the exact concentration of the initial solution using the following form of the Nernst equation:

$$C=\frac{C^{*}\,[(V_s/(V_x + V_s)]}{(\text{antilog}\ \Delta E/S)-[V_x/(V_x + V_s)]}$$

C=Sample concentration
C*=Concentration of addition before adding to sample
Vx=Sample volume
Vs=volume of addition
ΔE=potential difference between initial and final millivolt values with addition of standard.
S=millivolt span of electrode for decade of interest; i.e., the slope.
The units of C are μg/ml.
Therefore, Percent F =

$$\frac{[\mu g/ml\ (i.e.\ C)]\ (100\ ml)\ (100\ percent)}{(1000\ \mu g/mg)\ (wt.\ in\ mg)}$$

Report the values to two decimal places. A computer program is available for the above calculations on both the Tektronix 4051 and the HP-97.

12. When mv readings approach zero or cross to the negative axis, make another fusion in the usual manner. Add an aliquot of the solution to another beaker and dilute with an aliquot of acid to 50 ml. Continue with the determination as usual. The calculations are altered by considering the sample weight in mg present in the aliquot.

Compiled by M. Cremer

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DIGESTION METHOD FOR FLUORINE IN PHOSPHATE

(Adapted from Determining Fluoride in Rocks with a Specific Ion Electrode,
Blanche L. Ingram and Irving May, U.S. Geological Survey Professional Paper 750-B, p. B180-B184)

The phosphate rock sample is decomposed by digestion in dilute nitric acid. The solution is filtered; the residue is washed with 1 percent HNO_3; and the resulting filtrate is made to volume with water. An aliquot is transferred to another volumetric flask, a sodium citrate-potassium nitrate solution is added, and the combination made to volume with water. Standard fluoride solutions containing the same buffer are prepared for a calibration curve. Fluoride in all solutions is measured with a specific ion electrode.

Reagents (all chemicals-reagent grade):

0.6 M sodium citrate dihydrate - 0.2 M potassium nitrate solution. Dissolve 177 g of sodium citrate dihydrate and 20 g KNO_3 in water and dilute to one liter.

0.3 M sodium citrate - 0.1 M potassium nitrate solution. Dissolve 88.5 g of sodium citrate dihydrate and 10 g KNO_3 in water; add 2.5 ml 1 + 1 HNO_3 and dilute to 1 liter.

Standard fluoride solutions. Prepare standards containing 0.4, 0.6, 1, 2, 3, and 4 ppm F from 1000 ppm stock standard F solution using the 0.3 M sodium citrate - 0.1 M potassium nitrate solution as dilutent. Before making to volume, add 1+1 HNO_3 to match the unknowns; e.g. if 100 ml flasks are used, add ~ 0.3 ml to each flask.

Procedure	Comments
1. Digest 100 mg sample with 5 ml of 1 + 1 HNO_3 for a few minutes on the steam bath to decompose the sample.	
2. Filter the solution into a 100 ml volumetric flask. Wash the paper and residue with 1 percent HNO_3. Dilute to volume with water. Mix well.	
3. Transfer a 5 ml aliquot of the sample solution to a 100 ml volumetric flask.	3. Generally, fluorine in phosphate equals approximately 0.1 the phosphorus concentration. Therefore, this aliquot provides adequate fluorine--0.4 to 4.0 ppm.
4. Add 50 ml of 0.6 M sodium citrate - 0.2 M KNO_3 solution and dilute to volume with water. Mix well.	4. This provides a sample solution in 0.3 M sodium citrate - 0.1 M KNO_3 medium to match the standards. Aluminum interference is controlled by the citrate.

5. Starting with the lowest standard and proceeding to higher concentrations, measure the solution potentials as follows:

   Rinse the electrodes with distilled water and blot dry. Into a small plastic cap containing a small stirring bar, pour ~ 10 ml solution. Immerse the electrodes and check for and dislodge any air bubbles. Start gentle magnetic stirring. After 5 minutes, read and record the potential. Continue with the sample solutions in this manner.

6. Prepare a least squares curve from the standards' data. Compute percent F^- in the unknowns.

5. The selective ion electrode suffers from memory effects. Therefore, if a dilute solution is measured after a concentrated one, equilibration time is measureably increased.

6. The millivolt readings are treated as the independent variable. The log of the F^- concentration in ppm is the dependent variable.

Compiled by M. Cremer

FeO IN SILICATES, CARBONATES, AND PHOSPHATES, USING THE METROHM TITRATOR

Ferrous oxide (FeO) is determined by titration with standard dichromate solution using diphenylamine sulfonic acid as the indicator. A probe colorimeter is used.[6] The sample is decomposed by boiling with HF-H_2SO_4. The mixture is added to a phosphoric-boric-sulfuric acid solution to complex ferric and fluoride ions. The dissolution method only partially attacks pyrite, chromite, siderite, tourmaline, organic matter[5], and other related materials.[5,7] In the absence of complications, precision is within 0.1 percent (absolute), accuracy is ± 1 percent (relative), and detection limit is 0.02 percent FeO. Discussion of the procedure may be found in References 1, 4, and 7.

Reagent (all chemicals-reagent grade):

1:1:1 H_2O, 48 percent HF, 98 percent H_2SO_4
(300 ml each in a polyethylene bottle)

5 percent H_3PO_4 - 2 percent H_2SO_4 - 0.8 percent H_3BO_3 - (7800 ml H_2O, 390 ml H_3PO_4, 200 ml H_2SO_4, 65 g H_3BO_3 mixed in a large Pyrex dispenser bottle)

Sodium Diphenylamine Sulfonate: 0.1 percent aqueous solution

Potassium Dichromate: 0.1 N solution, prepared from NBS Standard No. 136b, at 20°C (9.8063g made to 2000 ml with H_2O)

FeO Spike: 0.1 N solution (~39.20 to 39.25 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, 5 ml H_2SO_4, made to 1000 ml with water)

Procedure	Comments
1. Weigh a 0.5 gram portion of the thoroughly mixed sample ground to pass 100 mesh. Transfer to a 50 ml platinum crucible which has a tightly fitting cover.	1. If the sample is ground much finer, surface area is increased which results in more exposure to the atmosphere. Some ferrous oxide can be oxidized to ferric oxide.

2. In a fume hood, and with a plastic graduate, add 13-14 ml HF-H_2SO_4 mixture to the crucible and immediately cover.

3. Quickly place the covered crucible on a silica triangle over a very small Bunsen burner with a flame about one-half inch high.

4. To bring the solution to a boil promptly, heat the crucible with a hand-held Tirrill burner, directing the flame toward the bottom and side, until a small, but steady flow of steam escapes from the crucible.

5. Remove the Tirrill flame and continue to boil gently for seven (7) minutes. The small flow of steam should continue throughout.

6. While sample is boiling, add 300 ml of the H_3PO_4-H_3BO_3-H_2SO_4 solution to a 600 ml beaker containing a Kel-F stirring bar.

7. Using a stirring rod to secure the lid, remove the crucible from the flame with Blair tongs; immerse the crucible and cover in the beaker containing the H_3PO_4-H_3BO_3-H_2SO_4 solution.

2. Hydrofluoric acid is a strong catalyst for the oxidation of ferrous sulfate in air. Therefore, the solution must be brought to a boil as soon as possible so that the air in the crucible is displaced by steam. The indicator may also be partially oxidized in the above solution. This condition produces an indistinct end point which occurs before the equivalence point. The problem is overcome with phosphoric acid which lowers the oxidation potential of the ferric-ferrous iron system by complexing with ferric ions.

   H_3BO_3 converts HF to fluoboric acid which removes the catalytic oxidation power of HF. Also attack on the glassware is minimized.

8.	Using the stirring rod or platinum tongs, remove and rinse the crucible, its cover, the tongs, and rod.	8.	The platinum-tipped tongs should not be immersed in the solution so deeply that the steel portion of the tongs is in the liquid.
9.	Add 8-10 drops of diphenylamine sulfonate indicator solution.	9.	At this point, the titration may be continued manually with a subjective decision as to the end point. This is definitely preferred when the FeO concentration is low, for the system tends to overtitrate in this instance. Only the titrator and stirrer need be activated.
10.	Turn on the four power switches. Block the probe light path by pacing the tip of a pencil between the mirror and the metal probe post. Turn the "TRANSMITTANCE ZERO" knob until the meter reads 0 percent transmittance.	10.	A 520 nm filter is used in the opening at the front of the probe colorimeter (PC/600).
11.	Place the beaker on the Metrohm Stirrer (E 549). Immerse the probe tip to a depth beyond the rectangular hole, but not beyond the top of the probe tip. If air bubbles appear in the probe tip opening, slightly agitate the probe sideways.		
12.	Position the $K_2Cr_2O_7$ dispenser tip so that the probe responds rapidly to the color of the stirred solution after each added drop.	12.	The dispenser tip should be placed as near as possible upstream (with reference to the stirring direction) from the probe.
13.	Turn the "ABSORBANCE ZERO" knob until the meter reads zero on the absorbance scale. Press START on the Titrator (E 526). The red pilot light goes out, and automatic titration begins. Note the stirring speed and adjust if necessary.	13.	The stirring speed must never be fast enough to scatter air bubbles from the vortex into the solution.
14.	Record the digital readout when the red pilot light comes on. Then continue with steps 15 and 16. If the readout is excessively small or the red pilot light never comes on, proceed to step 17.	14.	The purple color should persist for at least 30 seconds. However, the pilot light has come on after the time delay set on the titrator (30 seconds). If the end point is reached very soon or is never reached (the red light did not come on), either there is very little or no FeO or so much the titration takes a very long time. See Step 17.

15. Remove and rinse dispenser and probe; inspect the solids in the bottom of the beaker. A white powder is normal (SiO_2, CaF), but black specks and gritty particles are evidence of undecomposed sample. If this occurs, the determination should be repeated, using a smaller portion or one which has been more finely ground. Floating black particles indicate organic material. In the absence of undecomposed sample, reduce the data as follows:

$$\frac{\text{ml } K_2Cr_2O_7 \text{x } 0.1 \text{ N x } 71.84 \text{ x } 100 \text{ percent}}{\text{Sample Weight (milligrams)}}$$

$$= \text{Percent FeO}$$

Simplified:

$$\frac{\text{ml } K_2Cr_2O_7 \text{x } 718.4}{\text{Sample Weight (milligrams)}} = \text{Percent FeO}$$

Units:

$$\frac{\text{(ml) (meq/ml)(mg/meq)100}}{\text{mg}} \text{ percent} = \text{FeO}$$

16. If the analyst chooses, he may begin another sample (step 2) between steps 13 and 14.

17. With another portion of the same sample, repeat steps 1 through 9, only if the last sentence of step 14 is obtained.

18. Add 5.0 ml of the FeO spike solution and proceed with steps 10 through 15.

15. The dispenser should always be removed immediately to avoid alteration of the titrant by diffusion. In the event of undecomposed sample and/or organic material, the following note should be added at the end of the report: "Sulfides, refractory minerals, and organic materials, if present, prevent the accurate determination of FeO".

18. The spike solution guarantees an end point.

19. Standardize the spike solution three times by adding 5 ml to 300 ml of the H_3PO_4-H_3BO_3-H_2SO_4 solution to which indicator is added (see steps 6 and 9). Proceed through the remainder of the average in milleliters $K_2Cr_2O_7$ of the three titrations from the milliliters used for the spike plus sample. Proceed with the calculations in step 15.

19. Because the chemistry is not exactly matched, the (FeO) spike may exceed (FeO) spike plus (FeO) sample. In this case, it is assumed (FeO) sample is below the detection limit.

Compiled by P. Klock and M. Cremer

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7. Peck, Lee, 1964, Systematic Analysis of Silicates: U.S. Geological Survey Bulletin 1170, p. 39-42.

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DETERMINATION OF TOTAL Mn WITH $NaBiO_3$
(from Kolthoff and Sandell, p. 677)

This method is reported to be the most accurate for the determination of manganese when present in major concentrations (>1 percent). The sample is fused with Na_2O_2 and taken into solution with HNO_3 and H_2O_2. Following preliminary treatment with $NaBiO_3$ to destroy reducing substances, the Mn^{++} is oxidized to Mn^{7+} with bismuthate. A measured excess of ferrous salt is added to react with the Mn^{7+}, and the excess of Fe^{++} is then determined by titration with standard $KMnO_4$ solution.

Reagents (all chemicals–reagent grade):

Na_2O_2, powdered.

HNO_3, concentrated, boiled to removal of yellowish tinge of liquid and vapor phase. Nitrous acid must be absent. Prepare fresh daily.

1:30 HNO_3, prepared fresh daily, using boiled, cooled concentrated HNO_3 and boiled and cooled distilled H_2O.

$NaBiO_3$, powder. Available oxygen should correspond to at least 75 percent $NaBiO_3$. Chloride and manganese should be absent.

Standard solutions:

0.1000 N $K_2Cr_2O_7$. Prepared by dissolving 4.9035 g NBS sample No. 136c in boiled, cooled distilled water and diluting to 1000 ml at 20°C.

0.1 N $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$. Prepared from reagent grade crystals. Dissolve 39.2 g in 1 liter of 5 percent (v/v) H_2SO_4. Must be standardized daily using the 0.1000 N $K_2Cr_2O_7$.

0.1 N $KMnO_4$. Prepared from reagent grade $KMnO_4$. Standardized frequently by titrating with recently (same day) standardized $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (above).

Procedure	Comments
1. Weigh a 50-mg sample into a zirconium crucible.	
2. Add 0.5 g Na_2O_2 and mix by gently shaking.	
3. Fuse over a small Tirrill flame, taking care to avoid spattering. Set on a porcelain plate to cool.	

4.	Place crucible in a 250-ml beaker and cover with a watch glass.		
5.	With the beaker covered, add several ml distilled H_2O by squirting it into the crucible from a wash bottle through the beaker spout.		
6.	After vigorous reaction has subsided, remove watch glass and quickly add 5 ml boiled concentrated HNO_3 and a squirt of 30 percent H_2O_2. Replace watch glass.		
7.	Digest at steam bath temperature for about 2 hours. Cool to room temperature.		
8.	Add 0.5 g $NaBiO_3$ (if neither a precipitate nor a pink color is produced, add 0.5 g more bismuthate).	8.	Bismuthate is added to oxidize any reducing substances.
9.	Add dropwise a 6 percent solution of sulfurous acid (H_2SO_3) until color or precipitate disappears.	9.	Sulfurous acid is added to reduce all the manganese present to Mn^{++}.
10.	Add several glass boiling beads and boil 4-5 minutes.		
11.	Remove from heat and chill to 10°C in an ice bath. Add 10 ml of the boiled, concentrated HNO_3.	11.	Oxidation of the Mn will not be quantitative unless the sample is quite cold and the concentration of the HNO_3 is at least 10 percent and preferably 20 percent by volume. HCl and HF must be absent.
12.	Add 1 g $NaBiO_3$ and stir for 1-2 minutes. Some of the bismuthate should remain undissolved.	12.	The oxidation reaction of manganese to permanganate is: $2Mn^{+2} + 5 NaBiO_3 + 14H^+ \rightarrow 2 MnO_4^- + 5 Na^+ + 5 Bi^{+3} + 7 H_2O$.
13.	Add 50 ml <u>cold</u> 1:30 HNO_3 and mix.		
14.	Filter through two or more thicknesses of glass fiber paper into a wide-mouth 500-ml Erlenmeyer flask.	14.	To remove excess bismuthate filter the sample by placing the paper in a Buchner funnel which empties into the Erlenmeyer flask within a bell jar, which is attached to a vacuum pump. All contact of the sample with organic matter (such as paper or rubber) must be avoided.

15.	Wash the precipitate thoroughly with 1:30 HNO_3.	15.	Bismuthate shows a great tendency to retain permanganate.
16.	Add 3 ml concentrated H_3PO_4.	16.	H_3PO_4 is added to complex the Fe^{+3} formed during the titration. Thus the oxidation potential of the iron system is reduced, resulting in a sharp end point.
17.	Using a burette or a volumetric pipette, add an excess of the standard ferrous ammonium sulfate.	17.	A 50 mg sample which contains 74 percent MnO will require 30-40 ml 0.1 N $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$. The reduction reaction of permanganate to manganous salt is $MnO_4^- + 5Fe^{+2} + 8H^+ \rightarrow Mn^{+2} + 5Fe^{+3} + 4\ H_2O$.
18.	Titrate the excess Fe^{++} with the standard $KMnO_4$ to the first permanent pink tinge.		

Calculations:

I. From the normality of the $Fe(NH_4)_2(SO_4)_2.6H_2O$ solution, calculate the FeO equivalent of one ml $Fe(NH_4)_2(SO_4)_2.6H_2O$:

$$\frac{\text{mg FeO}}{\text{ml } Fe(NH_4)_2(SO_4)_2.6H_2O} = N_{Fe(NH_4)_2(SO_4)_2.6H_2O} \times 71.84$$

II. Calculate the FeO equivalent of one ml $KMnO_4$ solution:

$$\frac{\text{mg FeO}}{\text{ml } KMnO_4} = N_{KMnO_4} \times 71.84$$

III. Calculate the MnO equivalent of the $KMnO_4$ solution:

$$\frac{\text{mg MnO}}{\text{ml } KMnO_4} = N_{KMnO_4} \times 70.94$$

IV. $$\frac{\left[\left\{\text{ml } Fe(NH_4)_2(SO_4)_2.6H_2O \text{ added} \times \frac{\text{mg FeO}}{\text{ml } Fe(NH_4)_2(SO_4)_2.6H_2O}\right\} - \left(\text{ml } KMnO_4 \times \frac{\text{mg FeO}}{\text{ml } KMnO_4}\right)\right] \times 70.94}{71.84 \times 5} = \text{mg MnO}$$

V. $$\frac{\text{mg MnO} \times 100}{\text{sample wt in mg}} = \text{Percent MnO}$$

Compiled by S. Neil

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MERCURY IN ROCKS AND MINERALS

(Adapted from Determination of Sub-microgram quantities of mercury by atomic absorption spectrophotometry by W. R. Hatch and W. L. Ott, Analytical Chemistry, v. 40, no. 14, December 1968, p. 2085-2087.)

The sample is treated with sulfuric and nitric acid. Potassium permanganate, potassium persulfate, and sodium chloride-hydroxylamine sulfate are added. Lastly, stannous sulfate is added, and the vessel is immediately attached to a closed system apparatus. Mercury gas is liberated and carried by nitrogen through a quartz windowed tube. Absorbance of the emitted light from a hollow cathode mercury lamp occurs at 253.7 nm and is read with an atomic absorption unit.

Reagents (all chemicals-reagent grade):

Glassware used for the following mercury standards must be conditioned for approximately two weeks when the solutions are discarded and remade in the same glassware, rinsed only with distilled water.

Mercury stock solution-dissolve 0.1354 g of mercuric chloride ($HgCl_2$) in a mixture of 75 ml H_2O and 10 ml HNO_3. Dilute to 100 ml with H_2O. 1 ml = 1 mg Hg = 1000 ppm.

Mercury intermediate solution-pipet 2 ml of the stock mercury solution into a mixture of ~150 ml of water and 0.4 ml HNO_3. Dilute to 200 ml. Prepare fresh daily. 1 ml = 10 µg Hg = 10 ppm.

Mercury working solution-pipet 2 ml of the intermediate mercury solution into a mixture of ~150 ml of water and 0.4 ml HNO_3. Dilute to 200 ml. Prepare fresh daily. 1 ml = 0.1 µg Hg = 0.1 ppm.

Potassium permanganate solution-dissolve with heat 5 g potassium permanganate in water. Dilute to 100 ml with water.

Potassium persulfate solution-dissolve with heat 5 g $K_2S_2O_8$ in H_2O. Dilute to 100 ml.

Sodium chloride-hydroxylamine sulfate solution-dissolve 12 g of sodium chloride and 12 g hydroxylamine sulfate in H_2O. Dilute to 100 ml with water.

Sulfuric acid, 0.5N-14 ml concentrated H_2SO_4 to one liter H_2O.

Stannous sulfate solution-add 25 g stannous sulfate to 250 ml 0.5N H_2SO_4. This mixture is a suspension and must be stirred continuously during use.

Sulfuric-nitric mixture-add two parts concentrated H_2SO_4 to one part concentrated HNO_3.

Antifoam B-silicone emulsion.

Apparatus:

Atomic absorption spectrophotometer. Varien AA6 equipped with a recorder set at 0.5 inches/min.

Mercury hollow cathode lamp, Westinghouse, argon filled.

Absorption cell with quartz windows. Obtained from Varien.

Flowmeter calibrated in SCFH air units from 0 to 10.

Nitrogen high-purity carrier gas.

U tube filled with $CaSO_4$.

Gas washing bottle-250 ml capacity-equipped with a specially modified stopper to which is attached a 12-mm diameter fritted cylinder.

Tygon tubing.

<table>
<tr><th>Procedure</th><th>Comment</th></tr>
<tr><td>1. Weigh and transfer 0.2 to 1.0 g powder to a 250 ml Erlenmeyer flask equipped with a watch glass.</td><td>1. The weight is predicated upon the anticipated Hg concentration, the highest standard being 0.6 μg.</td></tr>
<tr><td>2. Add to the flask 7.5 ml 2:1 H_2SO_4-HNO_3 mixture. Reflux on a hotplate set at a temperature between 50°C and 95°C for two hours. Swirl the flask occasionally.</td><td>2. Hg in organic materials is reported to be stable at temperatures $\leq$ 50°C. In inorganic materials, it is reported to be stable at temperatures $\leq$ 95°C.</td></tr>
<tr><td>3. Cool. With a graduate, add 100 ml H_2O down the watchglass as well as down the sides of the flask.</td><td>3. Volumes throughout are kept at approximately 100 ml exclusive of added reagents.</td></tr>
<tr><td>4. Add 1 ml $KMnO_4$, swirl, and wait at least 15 minutes. If the purple color fades, add more $KMnO_4$.</td><td>4. Some samples containing organic material stubbornly fade even with 10 ml $KMnO_4$ and a pause of several hours. This has been found to result in a solution which foams uncontrollably when the carrier gas is applied.</td></tr>
<tr><td>5. After the purple color persists, add 2 ml $K_2S_2O_8$. Set aside overnight.</td><td>5. The addition of $K_2S_2O_8$ in addition to oxidant $KMnO_4$ guarantees the oxidation of organo mercury compounds. Mercury is stable in acid solution and in the presence of $KMnO_4$.</td></tr>
<tr><td>6. Next morning, prepare the following standards in duplicate in 250 ml Erlenmeyer flasks:
<table>
<tr><th>ml 0.1 ppm Hg solution</th><th>ml H_2O</th></tr>
<tr><td>0</td><td>100</td></tr>
<tr><td>2</td><td>98</td></tr>
<tr><td>4</td><td>96</td></tr>
<tr><td>6</td><td>94</td></tr>
</table>
Prepare one 10 ml-0.1 ppm Hg + 90 ml-H_2O to use to season the equipment.</td><td>6. Even for the standards, volumes are only approximate because standards and unknowns are treated exactly the same.
Micrograms of mercury are plotted as abcissa and absorbance as ordinate. Therefore, volumes do not enter into calculations.
Glass pipettes are used because mercury adheres to plastic.</td></tr>
<tr><td>7. Add to each standard 7.5 ml 2:1 H_2SO_4-HNO_3 mixture, 1 ml $KMnO_4$, and 2 ml $K_2S_2O_8$.</td><td></td></tr>
</table>

8. On the AA peak at 253.7 nm, align the cell, the lamp, etc., using absorption, A gain and slit 0.5 nm. Zero and calibrate the recorder.	8. A wide slit is acceptable because reduced mercury vapor in the absorption cell has very little spectral interference. Light output is increased and precision is improved.
9. Before beginning the analysis, turn on the N_2 gas and set the regulator to 20 psi. With the stopcock at bypass, the flowmeter should read 5 SCFH which converts to 3 SCFH when the carrier gas flows through the solution in the bottle.	
10. Pour the contents of the highest standard (i.e., the 1 μg) into the gas washing bottle. Rinse the Erlenmeyer flask sparingly three times. Pour the rinsings into the bottle. Add 2 ml NaCl-$(NH_2OH)_2 \cdot H_2SO_4$. Rapidly swirl the bottle. Check that the stopcock on the stopper is turned to by-pass. Insert the stopper in the bottle and secure the balljoints-one to the N_2 carrier gas, the other to the drying tube.	10. Upon being swirled, the solution becomes colorless. NaCl-$(NH_2OH)_2 \cdot H_2SO_4$ reduces excess $MnO_2{}^-$ and assures that free chlorine is absent before mercury is reduced.
11. Immediately add 5 ml $SnSO_4$ and close the system with a penny stopper.	11. The reduction reactions are: $2Hg^{++}+Sn^{++} = 2Hg^{+}+Sn^{++++}$ $2Hg^{+}+Sn^{++} = 2Hg+Sn^{++++}$ Because the couple Hg^{++}-Hg^{+} is a stronger oxidizing couple than Hg^{++}-Hg, the reducing agent Sn^{++}, present in excess, first reduces the mercuric ion and then the mercurious ion.
12. Start a stop watch. After 75 seconds, turn the stopcock to direct the carrier gas through the solution in the bottle.	12. The reduction reaction is reported to commence from 60 to 90 seconds after the addition of $SnSO_4$.

13. Note on the recorder trace the maximum absorption value. While waiting for the reading to descend to zero, transfer the 0.6 µg standard to the second gas washing bottle. Check that the reading is zero or thereabouts. Then turn stopcock to by-pass to vent any further mercury fumes. Disassemble the apparatus and rinse the $SnSO_4$ port, the stick, and the bottle three times with distilled H_2O.	13. The reading on the AA climbs to a maximum where it pauses and then descends to zero.
14. Proceed with the standards and unknowns in the foregoing manner, treating the standards in order of descending concentration. Average duplicate absorbance values. If the solution of an unknown forms and threatens to overflow, turn stopcock to by-pass until the foaming subsides. Again pass carrier gas through the solution. Switch the stopcock back and forth to vent the mercury up the hood. Disassemble the apparatus as described in step 13.	14. If the solution threatens overflow, absorbance cannot be determined. The sample and standards must be redone. One drop of antifoam B is added to both sample and standards just before the stopper is affixed to the bottle.
15. Prepare a second order equation by the least squares method, plotting µg mercury as abscissa and absorbance as ordinate. Use the equation to calculate the mercury concentration in micrograms of the unknowns. Convert to ppm remembering that the units of ppm are micrograms per gram.	15. Detection limit = 0.005 ppm. Perhaps the detection limit could be improved if ultra pure acids were used.

Compiled by M. Cremer

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AN EXTRACTION - COLORIMETRIC PROCEDURE FOR MOLYBDENUM

(A modification of the procedure of B. F. Quin and R. R. Brooks, published in Analytica Chimica Acta 74 (1975) 75-84, which in turn was a modification of the procedure of R. E. Stanton, published in the Proc. Aust. Inst. Min. Met., no. 235, Sept. 1970.)

The powdered sample is decomposed with HNO_3, $HClO_4$, and HF; taken to dryness; and brought up in HCl. The solution is transferred to a separatory funnel, and shaken with an ascorbic acid-citric acid reducing solution. Sodium iodide, thioglycollic acid, and zinc dithiol are added. The solution is mixed. The green molybdenum complex is extracted into isoamyl acetate, washed with a HCl-citric acid solution, and the absorbance read at 680 nm. The procedure allows for the determination of 0.1 ppm molybdenum.

Reagents (all chemicals-reagent grade):

Reducing solution. Prepare a solution containing 15 percent (w/v) ascorbic acid and 2 percent citric acid in distilled water.

Sodium Iodide solution. Prepare a 33 percent (w/v) solution of NaI in distilled water. Add 0.5 percent (w/v) ascorbic acid.

Zinc dithiol suspension. Add 5 ml of ethanol to 0.5 g zinc dithiol. Add 3 pellets NaOH (~1 g), 5 ml H_2O, and 0.5 thioglycollic acid. Mix well using a stirring rod to break up large pieces of zinc dithiol, and dilute to 100 ml with H_2O. The resulting suspension must be prepared fresh daily.

2N hydrochloric acid - 10 percent citric acid solution.

Thioglycollic acid (~48 percent).

Isoamyl acetate.

1000 ppm molybdenum standard solution. Dissolve 250 mg spec pure molybdenum powder in a measured volume of concentrated HNO_3. Let stand overnight at room temperature. Add concentrated HCl so that the ratio HNO_3:HCl is is 3:1. Evaporate to dryness. Take up with heat in a measured volume HCl. Cool. Make to 250 ml volume with H_2O and HCl if necessary, so that the solution is 20 percent HCl.

Procedure	Comments
1. Transfer 0.500 grams powdered sample to teflon crucibles.	
2. Prepare a series of standards 0.0 to 5.0 μg molybdenum by transferring each standard to a teflon crucible.	

3. Add to each crucible 1 ml $HClO_4$, 5 ml HNO_3, and 15 ml HF. Evaporate the solution to dryness on a hot plate set at approximately 150°C.	3. HNO_3 is added first to oxidize any organic material before $HClO_4$ comes in contact with it.
4. Add 15 ml 3N HCl, cover, and heat at 100°C until the salts are dissolved.	
5. Transfer the solution to a 60-ml separatory funnel, add 1.5 ml reducing solution, mix thoroughly, and let stand for 5 minutes.	5. Both Fe(III) and Cu(II) form dithiol complexes which are stable and insoluble in isoamyl acetate. Ascorbic acid reduces Fe(III) and Cu(II) to Fe(II) and Cu(I) respectively, thus preventing consumption of dithiol by these elements. The Fe(III)-dithiol complex is black, and the Cu(II) complex is purplish-black. Citric acid complexes tungsten which forms a blue-green complex with dithiol. Also see Comment 7.
6. Add 3 ml sodium iodide solution followed by 0.05 ml thioglycollic acid.	6. Sodium iodide precipitates Cu(I) as grey cuprous iodide. Thioglycollic acid slows the extraction of iodine into the isoamyl acetate.
7. Add 1 ml of zinc dithiol suspension, mix, and let stand for 5 minutes.	7. The white colloidal suspension which first forms is dithiol precipitate. Mo(VI) reacts with the dithiol to form a yellow-green complex. The standing period should be carefully timed in the unlikely event that any tungsten has escaped the citric acid.
8. Add 5.0 ml isoamyl acetate and extract the green molybdenum complex by shaking the separatory funnel for approximately 3 minutes. Drain and discard the aqueous layer.	8. After the transfer of the complex to the isoamyl acetate, the aqueous layer should be drained off, as dithiol is slowly decomposed oxidatively by iodine as more iodine extracts. Eventually the color of the iodine itself causes significant interference.
9. Wash the isoamyl acetate layer twice (~30 seconds each) with 5 ml portions of the HCl-citric acid solution, and discard the washes. Rinse the tip of the funnel with H_2O, insuring that the H_2O is drained from the tip completely.	
10. Let the solutions stand for 1/2 hour. Then drain the isoamyl acetate layer and read the absorbance of the solutions at 680 nm.	10. If the organic layer is cloudy due to the presence of dispersed H_2O droplets, place the separatory funnel into hot H_2O.
11. Analyze the data by the method of least squares.	

K_2O AND Na_2O ANALYSIS

(An unpublished method devised by C. O. Ingamells and amended by F. O. Simon and J. H. Christie)

Potassium and sodium, as the oxides, contribute substantially to the summation in a classical rock and mineral analysis. Potassium measurements are used in potassium-argon dating.[1]

The samples are fused in graphite with $LiBO_2$ and dissolved in 4 percent HNO_3. Lithium serves as an internal standard for the measurements which are made on a flame photometer.[2] A calibration curve is calculated using rocks and minerals previously analyzed by various primary methods. In the absence of complications, a precision of 0.1 percent absolute and a detection limit of 0.025 percent K_2O are attainable.[3]

Procedure	Comments
1. Based upon the rock description, decide whether high or low standards are to be used for the calibration curve (see attached list). Weigh each Standard in duplicate.	1. To extend the limited supply of standards 40-50 samples are run at one time. The division between "high" and "low" occurs at ~ 3.0 percent K_2O. All sodium calibration curves are calculated from the sodium values accompanying the chosen K_2O standards. Quality control samples are included in each run.
2. In a tared, size 00 black porcelain crucible weigh 100 ± 3 mg sample. Add 700 ± 5 mg of pure anhydrous $LiBO_2$. Record both sample weight and total weight. In the same crucible, mix the sample and flux.	2. Samples and standards are weighed on the same day because $LiBO_2$ is somewhat hygroscopic. The purity of each new batch of $LiBO_2$ is checked by emission spectroscopy.
3. Brush the interior of a high purity graphite crucible and transfer quantitatively the mixture to the graphite crucible. Store samples and standards in lucite trays.	3. The purity of each new batch of graphite crucibles is checked by firing one crucible to disintegration at 1000°C in a platinum dish. The residue, if any, is weighed and analyzed by emission spectrography. New crucibles must be ignited for 2 hours at 1000°C before being put into use.
4. Fuse the contents of the first six crucibles at 950°C for 15 minutes.	
5. During the fusion, equip six 250 ml tripour beakers with dry 1 5/8 inch Kel-F magnetic stirring bars. Label six cardboard covers. Add 100 ml of 4 percent v/v HNO_3; begin stirring in the solution[5], as the time approaches to remove the crucibles from the	

6. At the end of 15 minutes, slightly swirl the red hot crucible and pour the molten bead into its corresponding beaker. Place each emptied crucible in some noted order. Cover beakers tightly. Stir for ten minutes while fusing the next lot of six. Inspect the solutions for clarity.	6. Cloudy solutions may contain some reducible element; a drop of 30 percent H_2O_2, usually causes the solution to clear.
7. Inspect each cool graphite crucible for adhering particles.	7. Adhering particles, if any, must be dug out with a stainless steel spatula and added to the appropriate beaker. If this is not feasible, a new portion must be fused on another day. (See comment 2)
8. Repeat the above procedure for all samples.	
9. Use the automatic diluter to dilute samples 1 to 10, with distilled H_2O dispensing into small 15 ml plastic beakers.	9. The dilution need not be exactly 1:10 but it must be the same for all solutions.
10. On flame photometer, turn on both the propane gas and air completely, in that order.	
11. Depress power (flame will automatically ignite). Allow 45 minutes for warm up.	
12. Continually aspirate H_2O during warmup. For 5 minutes during the warmup, aspirate a dilute solution of reconstituted normal human blood serum. (1 drop per 25 ml H_2O)	12. The blood serum protein coats the spray chamber to minimize formation of water droplets on the chamber walls. Undiluted serum is kept refrigerated.
13. Before operating with rock solutions, check that the aspiration rate is approximately 40 seconds/ml.	

14. On the Digital Printer press reset to set the sequential counter to 001. Depress ADVANCE to position the paper.

15. For K_2O analysis, aspirate Sierra Quartz. Adjust the signal display on the lithium response meter so that the red needle comes to rest opposite the black triangle between the horizontal black lines. Set the digital concentration display to zero with the knob on the left side of the instrument.

16. Aspirate the highest K_2O standard. Check the lithium response and adjust if necessary. Using the dial at the left of the display. Set the digital concentration to < 280.0 (high scale) or < 28.0 (low scale) whichever is applicable.

17. If Na_2O has also been requested, repeat step 15.

18. Aspirate the highest Na_2O standard and switch to low scale because Na_2O is always run on that scale. Check lithium as before and set the percent Na_2O on the digital display. The decimal point appears between the 3rd and 4th digit.

19. Aspirate standards and unknowns in the following order, depressing DATA when the display no longer changes, usually after 8-10 seconds. All solutions must be read in the same manner.
Typical aspiration order:
    a. duplicate standards
    b. 6 unknowns
    c. duplicate standards
    d. the same 6 unknowns
    e. duplicate standards

16. The black switch to the right of the display activates the high and low scale. The setting chosen for the high standard is arbitrary. The settings suggested here allow for instrument drift since the full span is 0 to 280.0 or 0 to 28.0. The decimal point appears between the second and third digit (e.g. 17.00 for 1.70 percent K_2O); on the high scale it appears between the third and fourth digit (017.0).

19. Drift response is inherent in the operation of the flame photometer. Frequent aspiration of standards to bracket unknowns minimizes errors introduced by instrumental drift. A set of standards and unknowns should not exceed ten of each.

20. Continue the operation until all unknowns have been run. The data collected from 19a and c above is weight corrected and used to prepare a linear regression. From this slope-intercept equation the concentration of the unknowns in 19b is calculated and weight corrected. Data from 19c, d, and e are treated in the same manner. The reported value is the average of the two calculated values.

Compiled by M. Cremer

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DIVISION OF ROCKS INTO HIGH AND LOW % K_2O

LOW'S - % K_2O 3.0%

- Actinolite
- Alunite; Both high and low, 2-8%
- Amphibole
- Andesite
- Basalt
- Biotite-Camptonite; 2.5%
- Caliche (very difficult)
- Camptonite
- Chlorite
- Dacite; Both high and low, 2-4%
- Gabbro
- Granite
- Greenstone
- Hornblende
- Metagraywacke
- Plagioclase
- Pumice
- Quartz
- Quartz-Sericite; Both high and low, 1-6%
- Riebeckite
- Soil Carbonates
- Whole Rock

HIGH'S - % K_2O 3.0%

- Adularia (generally)
- Alunite; Both high and low, 2-8%
- Biotite
- Dacite; Both high and low, 2-4%
- Feldspar; (alkali; K-Feldspar, generally)
- Felsite; 4-6%
- Glauconite
- Glaucophane; Both high and low, see amphibole.
- Granodiorite; Both high and low 2-7%
- Monzonite: Both high and low, 2-6%
- Muscovite; Both high and low, to 7%
- Obsidian; (generally)
- Orthoclase; ?
- Perlite; 5%
- Phlogophite
- Phyllite
- Quartz-Sericite; Both high and low
- Rhyolite; ? Both high and low?
- Sanidine; 13%
- Sericite; 0.5-5%
- Syenite; 4%
- White Mica

MICROCOULOMETRIC MEASUREMENT OF WATER IN MINERALS

When sample quantity is a problem, total water is determined on 50 mg or less using the Dupont Moisture Analyzer which has been modified to accommodate decomposition outside the instrument. Nitrogen gas carries the water from the melted sample and flux in the combustion tube to the electrolytic cell. The cell current integrating system is calibrated to read directly in micrograms. The reaction in the cell is:
$P_2O_5 + H_2O_{(g)} \rightarrow P_2O_5 \cdot H_2O \rightarrow P_2O_5 + H_{2(g)} + 1/2\ O_2(g)$.

Reagents (all chemicals-reagent grade):

Calcium carbonate powder.

Körbl combustion catalyst (silver permanganate decomposition product) either purchased or prepared from potassium permanganate and silver nitrate.

Lead oxide yellow (low silver) powder, lead chromate powder, and copper oxide powder.

Apparatus:

A modified Dupont Type 26-321A-MA Moisture Analyzer.

Dry cylinder nitrogen (99.995 percent purity, dew point - 90°F).

Two solid acrylic purge meters (flowmeter), Matheson Series 201.

Large $CaSO_4$ drying tube.

U tube filled with magnesium perchlorate (a.k.a. anhydrone).

Stopcock grease, not high vacuum.

Vycor microcombustion tube with bent capillary side arm.

Teflon tubing.

Silica wool.

Micro combustion furnace controlled by a variable transformer.

Coors no. 00 porcelain boats.

Aluminum tray to hold Coors boats.

Silicon stopper.

Procedure	Comment
1. Clean in the usual manner and then ignite Coors No. 00 porcelain boats for 1/2 hour at 1000°C. Store in a desiccator.	1. After choosing the combustion tube, test each boat for fit.
2. Clean combustion tube in the usual manner. Do not handle with bare hands. Dry overnight at 105°C.	2. Fingerprints on heated quartz hasten devitrification.
3. Prepare a 10 + 1 + 1 PbO:$PbCrO_4$:CuO flux by intimate mixing and ignition for 30 min at 400°C. Store in desiccator.	
4. Dry the Körbl combustion catalyst and the $CaCO_3$ for several hours at 105 ± 5°C. Add to the combustion tube a plug of silica wool-Körbl combustion catalyst-silica wool-calcium carbonate-silica wool a few inches from the reduced end.	4. The Körbl combustion catalyst insures the oxidation of organic compounds and hydrogen. Calcium carbonate absorbs acid gases which otherwise corrode the tubing and flow control.
5. Place the combustion tube in a rack holding a combustion furnace to which a Variac is attached. Raise or lower the combustion tube in the rack so that it is centered within the furnace element. Then make the following connections: Nitrogen tank → tygon tubing → flow meter → tygon tubing → Drierite → tygon tubing → magnesium perchlorate in U tube → tygon tubing → moisture analyzer → teflon tubing → combustion tube → teflon tubing → moisture analyzer oven → teflon tubing → cell → latex tubing → flow meter.	5. The nitrogen tank should be equipped with a regulator and metering valve. None of the tubing should be unnecessarily long. The connecting tubing at the back of the moisture analyzer should be as short as possible; i.e. the pyrex outlet from the U tube should extend into the metal inlet hole on the moisture analyzer. The junction is secured with a clamp around a piece of tygon tubing which is screwed onto the moisture analyzer threads.
6. Set the delivery pressure on the regulator to ~5 psiq. With the metering valve, set the flow to ~0.05–0.06 SCFH air.	
7. Insert an exhausted cell in the cell case and check the flowmeter at line's end.	7. The flowmeter should read approximately the same as the entrance flowmeter. If it does read too low or not at all, the whole system must be checked for leaks using Snoop solution. If no leaks appear, then the capillary in the cell is blocked; another cell should be inserted.

8.	When the system is leak free, purge with N_2 for ~15 minutes or longer. Install a functioning cell and again dry the system for an hour or until the zero adjust control can be set so the count rate falls between 15 counts/15 seconds and 45 counts/15 seconds.	8.	See paragraph 2-8, p. 2-2, Operation and Maintenance Manual, Type 26-321A-Moisture Analyzer. With the timer off, press and hold down the zero pushbutton to adjust the count with the knob at the right.
9.	Attach a recorder to the moisture analyzer.	9.	It is helpful to follow cell performance with a recorder.
10.	Each morning, or after a lengthy interruption, burn out the system by heating the right side of the combustion tube to ~1100°C by turning the Variac to ~135. At the same time, turn the timer on the moisture analyzer to one hour.	10.	Moisture buildup can occur over an inactive period of about an hour. The moisture analyzer is set so that the temperature within its oven is ~450°C. The Variac has been calibrated against the temperature in the combustion tube.
11.	After 15 minutes, turn the Variac to 65 and allow the furnace to cool ~8-10 minutes. Then move it over the plug of compounds.	11.	The temperature should have cooled to ~450°C in the 10-minute interval. The temperature was arbitrarily chosen to drive all H_2O forward without decomposing or melting the compounds.
12.	When the count subsides to ~1 count/6 sec., turn off the timer and the Variac. Or, if preferred, when recorder trace tails off and counting slows measureably, an arbitrary line on the trace can be chosen for turnoff. This line is then used in all subsequent operations.	12.	At this time, the moisture analyzer oven returns to ambient temperature, and the red proceeding light goes out. The analyzer is now ready to accept a blank or sample.
13.	While waiting for the moisture analyzer to complete its cycle after turnoff, check instrument and cell performance as follows: Choose as a standard a pure mineral whose water content has been determined by the Penfield method. Accurately weigh a boat, remove it from the balance to the small aluminum tray, and fill the boat with ~50 mg of the mineral. Use <50 mg if the water content is >5 percent. Reweigh boat and sample.	13.	So that the determination can be made in a finite time, a readout of ~2000 to 3000 μg water should not be exceeded, if possible.

14.	Remove boat and sample and again place in aluminum tray. Fill boat with flux evenly distributed and reweigh.	14.	Filling the boat with flux usually results in an ~10 to 1 ratio flux to sample.
15.	Place the boat in the combustion tube near the right; center the furnace around it, and turn the Variac to 135. At the same time, turn the timer to one hour.		
16.	At the end of 15 minutes, turn the Variac to 65 and allow 8-10 minutes cooling.	16.	During this period, a pattern of peaks appears on the recorder paper which differs with mineral type, amount of sample and flux, amount of packing in combustion tube, etc.
17.	Then move the furnace all the way to the left of the rack around the compounds.	17.	Now the major peak appears--that water trapped by the compounds.
18.	When the count matches that of step 12, turn off the timer and the Variac. Record μg of water.	18.	The recorder pen will now be back at its beginning position.
19.	In the same manner, weigh flux only to be used as a blank. Repeat steps 15-18. Record μg water and calculate the blank as percent H_2O: (μg H_2O) (100 percent)/wt in grams x 10^6.	19.	The blank is usually $\leq$ ~.03 percent H_2O.

20. Calculate percent water in the sample as follows:

$$\% H_2O = \frac{\left[(\mu g H_2O_{\text{mineral}}) - (\% H_2O_{\text{blank}} \times \text{flux wt. in } \mu g_{\text{mineral}})\right]\left[100\%\right]}{\text{grams mineral} \times 10^6 \frac{\mu g}{\text{gram}}}$$

21.	Repeat the determination twice more.	21.	Results should agree to approx. ±1 percent with each other and with the Penfield number.
22.	Determine H_2O in the unknowns in the same manner.		
23.	Soak used boats in concentrated HCl for three weeks. Scrape the boats and leach them in distilled H_2O until needed.	23.	The substances in the boats are converted to chlorides.
24.	To shut down the system, remove the cell, cap it, and store it in a desiccator. To bleed the N_2, remove the stopper next to the back of the moisture analyzer. Replace the stopper when the regulator reads zero.	24.	The gas is bled slowly so that particles are not blown into the flow system.

25. To recoat a cell, pass acetone and distilled H_2O through the cell parts three times alternatively. Finish with acetone. Prepare an 8-part acetone to a 2-part H_3PO_4 mixture. Pass 2 ml through the cell. To convert the mixture to P_2O_5, connect the cell to the system. Turn the moisture analyzer to one hour and purge with dry N_2. The process, according to Dupont, may take from 15 to 45 minutes.

Compiled by M. Cremer

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