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Standard Reference Materials:

METHODS OF ANALYSIS OF NBS CLAY STANDARDS

U.S.
DEPARTMENT
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Standard Reference Materials:

Methods of Analysis of NBS Clay Standards

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PREFACE

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FOREWORD

This publication describes an effective combination of classical and instrumental analytical chemistry in characterizing a complex natural product. The attainment of accuracy in such an analysis requires the careful evaluation of systematic errors and the application of appropriate corrections. Specifically, in the gravimetric procedures, corrections for solubility and/or co-precipitation of impurities were determined by spectrophotometric procedures. Similarly, the selection of calibration procedures and standard addition methods in flame spectroscopy reduced the uncertainty in establishing values for minor and trace elements. These data have led to the certification of SRM's that were much needed for the rapid analysis by newer methods such as X-ray fluorescence. The latter methods, while precise, suffer from matrix effects which require appropriate standards to calibrate these instruments.

METHODS OF ANALYSIS OF NBS CLAY STANDARDS

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This publication brings together a compilation of
methods used at NBS for the analysis of two complex
standard reference clay materials. The methods were
selected to give the best obtainable results for those
elements normally found in clays. In some instances,
more than one procedure was employed for an element as
a cross-check on the precision and accuracy of the
results. The procedures are presented in two parts.
Part I is concerned with the determination of the major
constituents by the classical analytical procedures.
Part II covers the minor elements which are determined
instrumentally by flame emission and atomic absorption
spectrometry. These clay materials serve as analytical
composition standards to provide quality control of the
basic raw materials which are used in the ceramics and
refractories industries.

Key words: Atomic absorption; ceramics; classical
            procedures; clay materials; flame emission;
            refractories; Standard Reference Materials.

INTRODUCTION

The published methods of analysis for clays and similar
silicate materials, though fairly extensive, are widely scat-
tered. This publication endeavors to bring together a compila-
tion of methods used at NBS for the analysis of two complex
standard reference clay materials, plastic and flint. The
methods were selected and designed to give the best obtainable
results for those elements normally found in clays. In some
instances, more than one procedure was employed for an element
as a cross-check on both the precision and accuracy of the
results. The procedures are presented in two parts. Part I
is concerned with the determination of the major constituents
by the classical analytical procedures. Part II covers the
minor elements which can most conveniently be determined in-
strumentally by flame emission and atomic absorption spectro-

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etry. These latter procedures are attractive because of their speed, high sensitivity and improved precision and accuracy over the older and more time-consuming methods.

With issuance of these two Standard Reference Materials, NBS is providing renewals of materials that were first issued in 1931. These materials serve as analytical composition standards to provide quality control of the basic raw materials that are used in the ceramics and refractories industries. They will also serve as controls for the calibration of many instrumental methods. Marked advances, in recent years, in both instrumental and analytical techniques that are applicable to these materials, emphasize the need for well characterized standards.

These natural occurring materials have complex compositions and the classical analytical procedures are both time-consuming and difficult. To emphasize their difficulty, Lundell and Hoffman [1], as early as 1928 provided data to show the lack of agreement between analysts who assisted in the cooperative analysis of similar materials. More recently, in 1969, Flanagan [2] of the U.S. Geological Survey reiterated that the problem still exists.

The preparation of the materials, prior to sampling for analysis, consisted of sifting through a 50-mesh sieve and then mixing in a mechanical double-cone porcelain-lined mixer for a total of 2 hours. Homogeneity for each of the clays was established by an extensive sampling procedure conducted by S. D. Rasberry of the Spectrochemical Analysis Section of the Analytical Chemistry Division. Four main samples and 4 sub-samples were tested by x-ray fluorescence for the major elements. Sixteen replicate analyses were performed for silicon, aluminum, iron, titanium, calcium and potassium. The major elements and minor constituents were then determined by gravimetric, titrimetric, spectrophotometric, flame-emission and atomic absorption methods. The loss on ignition was based on heating the dried samples for 2 hours at 1100 °C.

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SILICA

Silica is an important constituent of clays, generally amounting to one-fifth to two-thirds of their composition. Most of the methods for the determination of silicon are gravimetric procedures in which the silicon is converted to a soluble form by fusing with Na_2CO_3, Na_2O_2, $K_2S_2O_7$, or $Na_2S_2O_7$. Satisfactory fusions are obtained by using equal parts of Na_2CO_3 and fused $Na_2B_4O_7$, but the $Na_2B_4O_7$ must be removed before making determinations of silica or alumina. A satisfactory fusion is also obtained with anhydrous lithium metaborate.

In clays, virtually all of the silica exists in the combined form as aluminum silicate, iron silicate, and potassium aluminum silicate.

SILICA BY THE HYDROCHLORIC ACID DEHYDRATION-(GRAVIMETRIC) METHOD

I. Scope

This method covers the determination of silica in concentrations from 20 to 70 percent. The relative standard deviation is 0.2 percent.

II. Principle of Method [3]

After fusion of the sample, silicon is converted to silicic acid with hydrochloric acid and made insoluble by double dehydration. The solution is filtered, and the silica is ignited, weighed, and then volatilized with hydrofluoric acid. The residue is ignited and weighed. The loss in weight represents silica (SiO_2). Soluble silica in the filtrate is determined by spectrophotometry and combined with that found by gravimetry.

III. Interferences

Silica is contaminated with alumina, titania, zirconia or their phosphates, but the contaminants do not interfere

since they are weighed after the treatment of the impure
silica with sulfuric and hydrofluoric acids.

IV. Procedure

   (a) Transfer approximately 1g of sample to a weighing
bottle and dry for 2 hrs at 140 °C. Stopper the bottle
and cool for 1 hr in a desiccator. Lift the stopper for an
instant, replace, and weigh the bottle and sample. Transfer
the sample, without brushing, to a 25 ml platinum crucible
containing about 1.25g of anhydrous Na_2CO_3. Reweigh the
bottle. The difference is the weight of the sample.

   (b) Thoroughly mix the dried sample and Na_2CO_3 by
stirring with a platinum rod. Add another 1.25g portion
of Na_2CO_3 and mix. Repeat with a third portion of Na_2CO_3
and mix. Use 1.25g of the Na_2CO_3 to clean the stirring
rod and then cover the mixture. Heat the covered crucible
over a low flame for several min and gradually increase
the heat until the mass is molten. Using tongs, slightly
tilt and rotate the crucible to fuse any particles which
may cling to the side of the crucible above the liquid.
Heat over an open flame for 20 min. Tilt and rotate
the crucible to spread the melt around the inside of the
crucible and cool. Gently heat the crucible over an
open flame for 30 secs, and cool.

   (c) Cover the fused sample with water, transfer
the contents to a platinum dish or Teflon beaker and wash
the inside of the crucible and the lid. Cover the fusion
with water and allow to stand overnight. Reserve the
crucible.

   (d) Pulverize the cake and stir the solution. Place
the tip of a funnel under the cover of the dish or
beaker. Add 5 ml of HCl to the reserved crucible. Slowly
and cautiously, pour 40 ml of HCl (1+1) through the
funnel. Transfer the contents of the reserved crucible
through the funnel. Rinse the crucible and cover with

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water and HCl repetitively. Wash the funnel and funnel tip, and remove.

(e) Allow the solution to stand until reaction ceases. Rinse the cover, replace it on the dish or beaker and heat on a steam bath until carbon dioxide is expelled. If any insoluble residue is present, filter, wash the residue with water, transfer the paper to the crucible used for the fusion, and ignite at low heat until carbon is removed. Fuse the residue with 2g of Na_2CO_3 and add the cooled melt to the original solution. Wash the cover and replace it on the dish or beaker containing glass hooks or a triangle and evaporate the solution to dryness with occasional stirring.

(f) Add 50 ml of HCl (1+4) to the dish or beaker, cover, and heat for 10 min. Add 150 ml of hot HCl (1+19), stir to dissolve salts, and filter immediately by decantation through a 11-cm medium filter paper into a 600 ml beaker. Wash the residue once with 15 ml of hot HCl (1+19). Transfer the bulk of the silica to the funnel. Scrub the dish or beaker thoroughly with a rubber-tipped rod. Wash the paper and precipitate 15 times with hot HCl (1+19) and 3 times with hot water. Transfer the paper and contents to a platinum crucible and reserve.

(g) Transfer the filtrate and washings to the original platinum dish or beaker. Evaporate to dryness on a steam bath. Add 50 ml of HCl (1+4), digest and filter through a 9-cm fine filter paper. Scrub and wash the container 10 times with hot HCl (1+19) and 3 times with hot water. Reserve the filtrate (A) and washings after evaporating to about 200 ml for spectro-photometric determination of soluble silica.

(h) Transfer the paper to the reserved platinum crucible, dry and heat slowly to 600 °C until the

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carbon is removed. Finally ignite for 1 hr at 1200 °C
to constant weight. Cool in a desiccator, and weigh
after 30 mins.

(i) Add about 1 ml of water and 6 drops of H_2SO_4
(1+1) to the SiO_2 precipitate. Add 15 ml of HF and
evaporate to dryness and then heat at a gradually
increasing rate until H_2SO_4 is removed. Ignite for
10 min at 1100 to 1150 °C, cool in desiccator, and
weigh. The difference is the weight of silica.

V.   Calculation

Calculate the percentage of silica as follows:

$$\text{Silica, percent} = \frac{A-B}{C} \times 100$$

where:

    A = initial weight, in grams, of crucible and
        impure SiO_2.
    B = final weight, in grams, of crucible and residue.
    C = grams of sample used.

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SOLUBLE SILICON FOLLOWING SILICA DEHYDRATION

Separation of silicon by dehydration with acid is never complete because of the solubility of silicic acid. Soluble silica in the filtrate from the dehydration may be determined spectrophotometrically.

The molybdenum blue method is a useful method for the photometric determination of silicon up to 200 parts per million. Molybdisilicic acid formed in a solution containing hydrofluoric, boric, and molybdic acids at pH 1.7 to 1.8 is extracted with butyl alcohol after addition of tartaric acid. The heteropoly acid is reduced with stannous chloride to the blue complex before measuring the intensity of the color. The addition of tartaric acid prohibits further reactions of the molybdisilicic acid with the silica from reagents or glassware.

SILICON BY THE MOLYBDENUM BLUE-(PHOTOMETRIC) METHOD

I. Scope

This method covers the determination of silicon in concentrations from 5 to 200 ppm in filtrates from silica separations in clays. The standard deviation at this range is 0.0001 percent.

II. Principle of Method [4]

The filtrate from the dehydrated silica is treated with hydrofluoric, boric, and molybdic acids and adjusted to a pH of 1.7 to 1.8. Molybdisilicic acid is extracted with normal butyl alcohol and reduced to a heteropoly blue complex. The spectrophotometric measurement is made at 635 nm.

III. Interferences

The elements normally present in clays do not interfere. Solutions should be kept in plastic containers.

IV. Concentration Range

The recommended concentration range is from 5 to 20 µg of silicon per 50 ml of butyl alcohol, using a 2-cm cell.

V. Stability of Color

The color is stable for at least 1 hr.

VI. Reagents

(a) Ammonium Hydroxide Solution. Bubble ammonia gas using plastic tubing, into cooled distilled water in a polyethylene bottle until the solution is saturated.

(b) Boric Acid Solution (50g/l). Dissolve 50g of H_3BO_3 in 900 ml of warm water, cool, and dilute to 1 liter with water.

(c) Potassium Permanganate Solution (0.6g/l). Dissolve 0.15g of $KMnO_4$ in 200 ml of water and dilute to 250 ml with water.

(d) Molybdic Acid Solution. Dissolve 25g of ammonium molybdate tetrahydrate in 200 ml of H_2SO_4 (1+9) in a 400-ml plastic beaker, dilute to 250 ml with water, and filter through a close-textured paper in a plastic funnel into a polyethylene bottle.

(e) Tartaric Acid Solution (200g/l). Dissolve 50g of tartaric acid in 200 ml of water and dilute to 250 ml with water.

(f) Stannous Chloride Reducing Solution (20g/l). Dissolve 2g of $SnCl_2.2H_2O$ and 1 mg of $CuCl_2.2H_2O$ in 100 ml of HCl (sp. gr. 1.18) and store in a glass-stoppered bottle. This solution should be prepared fresh every 3 days.

(g) Silicon, Standard Solution (A) (1 ml ≃ 200 µg of Si). Fuse 213.9 mg of SiO_2 with 2g of Na_2CO_3 in a platinum crucible, cool, and dissolve the melt in 200 ml of water in a plastic beaker. Transfer the solution to a 500-ml

volumetric flask, dilute to the mark with water, mix well, and store the solution in a plastic bottle.

(h) Silicon, Standard Solution (B) (1 ml $\approx$ 2 µg of Si). Transfer exactly 10 ml of standard silicon solution (A) to a 1-liter volumetric flask, dilute to the mark with water, mix well, and store in a plastic bottle.

(i) Dilute Hydrochloric Acid (20% HCl). Add 100 ml of HCl (low in Si), in a plastic graduate, to 300 ml of water in a plastic bottle, mix, and cool. Dilute to 500 ml with water, and mix.

VII. Preparation of Calibration Curve

(a) Calibration solutions.

(1) Transfer 0.0, 2.5, 5.0, 7.5, and 10.0 ml of standard silicon solution (B) to five covered 250-ml plastic beakers. Add 10 ml of the 20% HCl solution.

(2) Add 0.5 ml of HF, mix, and allow to stand several minutes. Add 40 ml of the boric acid solution and 4 ml of the molybdic acid solution, mixing after each addition. Add 3 or 4 drops of the potassium permanganate solution, mixing after each drop. Add 1 or 2 ml of the ammonium hydroxide solution from a plastic dropper to neutralize some of the acid before using the glass electrode. Adjust the pH of the solution to 1.7 to 1.8 with the ammonium hydroxide solution. Cover the beaker and heat for 10 minutes on a steam bath. Cool in water at 20 °C for 10 minutes. Add 4 ml of the tartaric acid solution and mix thoroughly. Glassware can be used from this point. Transfer the solution to a 250-ml separatory funnel. Wash the beaker twice with water and add the water to the funnel. Dilute the solution to a volume of approximately 90 ml, add 14 ml of H_2SO_4 (1+1), and mix. Cool to room temperature, add 50 ml of butyl alcohol, and shake vigorously for 1 minute. Allow the layers to separate, drain, and

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discard the acid layer. Wash the butyl alcohol layer by adding 20 ml of H_2SO_4 (1+99) to the separatory funnel, shaking for 30 seconds, allowing the layers to separate. Drain and discard the acid layer. Repeat the washing 2 more times. Transfer the butyl alcohol to a 50-ml volumetric flask. Wash the funnel twice with small portions (1 or 2 ml) of butyl alcohol and add the washings to the volumetric flask. Add 0.5 ml of the stannous chloride reducing solution to the flask, dilute to the mark with butyl alcohol, and mix.

(b) Spectrophotometry. Fill the reference cell with normal butyl alcohol and adjust the photometer to the initial setting, using a light band centered at approximately 635 nm. While maintaining this photometric adjustment, take the photometric readings of the solutions. One or two drops of the stannous chloride reducing solution may be added to the sample, mixed, and another photometric reading taken to check for the complete reduction of the molybdisilicic acid.

(c) Calibration curve. Plot the photometric readings of the calibration solutions against the micrograms of silicon per 50 ml of solution (Note 1).

VIII. Procedure

(a) Transfer the reserved filtrate of Section IV (g) of Dehydration-Gravimetric Method for Silica, see page 3, to a 250 ml volumetric flask, dilute to volume with water and mix. Using a plastic pipet, transfer a 4.0 ml aliquot to a plastic covered 250-ml plastic beaker and add 10 ml of 20 percent HCl. Proceed as directed in Section VII (a) (2) and (b).

(b) Carry a reagent blank following the same procedure and using the same quantities of all reagents.

(c) By means of the calibration curve, convert the spectrophotometric reading of the sample solution to micrograms of silicon.

IX.   Calculation

Calculate the percentage of silica as follows:

$$SiO_2, \text{ percent} = \frac{(A-B) \times 2.14}{C \times 10}$$

where:

A = micrograms of Si in 50 ml of butyl alcohol extract
    of the aliquot portion of the sample.

B = micrograms of Si in 50 ml of butyl alcohol extract
    of the blank.

C = gram of sample in 50 ml of butyl alcohol
    extract of the sample.

Add the silica percent obtained by spectrophotometry to
that obtained by gravimetry for the total percent silica
in the sample.

Note 1 - Plot absorbance A, against the respective
concentrations on ordinary graph paper; or concentration C,
against percentage transmission on semi-logarithmic paper
using the semi-log scale for the percentage T values.

ALUMINA

Alumina is an important constituent in clays; with silica it constitutes more than 82 percent of the clay standards. An accurate determination of aluminum in rocks, minerals and ceramic or metallurgical products is difficult for the analyst. Care must be taken to avoid contamination of aluminum with iron, titanium, zirconium, vanadium, phosphorus, and silicon. Improper ignition of the aluminum hydroxide precipitate and erroneous corrections for the impurities in the ignited product are sources of error. The caustic-citrate-cyanide-8-quinolinol-gravimetric method eliminates contamination of the aluminum precipitate, which is dried in an oven, and thus avoids the necessity of an ignition at high temperature.

In another method for alumina in clays, the sample solution is divided into three aliquots. In the first aliquot, Al_2O_3, Fe_2O_3, TiO_2, ZrO_2, P_2O_5, Cr_2O_3 and V_2O_5 are precipitated with NH_4OH. In the second aliquot of the same volume, Fe_2O_3, TiO_2, ZrO_2 and V_2O_5 are precipitated with cupferron. In the third aliquot, P_2O_5 is determined. Al_2O_3 is then determined by difference.

ALUMINA BY THE SODIUM HYDROXIDE-CITRATE-CYANIDE-8-QUINOLINOL-(GRAVIMETRIC) METHOD

I. Scope

This method covers the determination of alumina in concentrations from 20 to 70 percent. The relative standard deviation is 0.2 percent.

II. Principle of Method [5]

Silicon is separated with hydrofluoric acid. Titanium, iron and zirconium are separated with sodium hydroxide. The alkali salts and magnesium are removed with ammonium hydroxide and aluminum is then precipitated with 8-quinolinol in an ammoniacal solution containing ammonium citrate, hydrogen peroxide and sodium cyanide and weighed.

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III. <u>Interferences</u>

Aluminum is separated from phosphorus, arsenic, fluorine and boron by precipitation with 8-quinolinol in an ammoniacal solution. Titanium, vanadium, chromium, molybdenum, tantalum, and niobium do not interfere if precipitation is made in ammoniacal solutions containing hydrogen peroxide. Iron, copper, cobalt, nickel and zinc form complex ions with cyanide in ammoniacal solutions containing alkali cyanide and do not interfere.

IV. <u>Reagents</u>

(a) Citric Acid Solution (500g/l). Dissolve 50g of citric acid monohydrate in 50 ml of warm H_2SO_4 (1+49), dilute to 100 ml with water, and filter.

(b) 8-quinolinol Solution (80g/l). Dissolve 8g of 8-quinolinol in 12 ml of acetic acid, dilute to 100 ml with water at 60 °C, cool and filter.

(c) Cyanide Solution (400g/l). Dissolve 40g of NaCN in 50 ml of warm water, dilute to 100 ml with water, and filter.

(d) Ammonium Hydroxide Solution. Bubble ammonia gas, using plastic tubing, into chilled distilled water in a polyethylene bottle until the solution is saturated.

(e) Hydrogen Peroxide-(3 percent).

(f) Wash Solution-(2 percent). Dissolve 20g each of ammonium tartrate, sodium cyanide, and ammonium chloride in 1-liter of water.

V. <u>Procedure</u>

(a) Transfer approximately 0.5g of sample (use a sample weight containing not more than 0.1g of aluminum) to a weighing bottle and dry for 2 hrs at 140 °C. Stopper the bottle and cool 1 hr in a desiccator. Lift the stopper momentarily, replace, and weigh the bottle and sample. Transfer the sample, without brushing to a 1-liter platinum dish. Reweigh the bottle.

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(b) Add 15 ml of water, 10 ml of H_2SO_4, 15 ml of HNO_3, and 12 ml of HF to the covered dish and mix. Digest on a steam bath for 30 min with occasional stirring. Remove and wash the cover. Rinse the wall of the dish thoroughly and evaporate the solution to fumes of H_2SO_4. Cool, rinse the wall of the dish, mix and again evaporate to fumes of H_2SO_4. Cool, wash, mix and evaporate again. Complete removal of fluorine is essential. Cool, cautiously add 100 ml of warm water, and heat until the salts are in solution. Add paper pulp and filter through a 9-cm fine filter paper into a 600-ml beaker. Wash the paper thoroughly with hot water, and reserve the filtrate (A).

(c) Transfer the paper and residue to a platinum crucible and ignite at 600 °C. Cool, add 2 ml of water, 5 ml of H_2SO_4 (1+1) and 5 ml of HF. Evaporate to fumes of H_2SO_4 on a sand bath. Cool, wash the wall of the crucible with water, mix and evaporate to fumes of H_2SO_4. Cool, add 15 ml of water, mix, heat, and filter through a 7-cm fine filter paper containing paper pulp. Wash thoroughly with hot water. Combine the filtrate with the reserved filtrate (A).

(d) Transfer the paper and residue to a platinum crucible and ignite at 600 °C. Cool, add 0.6g of Na_2CO_3, cover and fuse over an open flame for 20 min. Cool, add 15 ml of water, and digest on a steam bath. Transfer the contents to a 250-ml Teflon beaker or a platinum dish, cover, and add 10 ml of H_2SO_4 (1+1). Heat on a steam bath to expel CO_2. Remove and rinse the cover. Rinse the wall of the beaker or dish, add 5 ml of HF, mix and evaporate to fumes of H_2SO_4. Cool, rinse the wall of the beaker with water, mix, and again evaporate to fumes. Cool, add 25 ml of water, heat, and combine the solution with reserved filtrate (A).

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(e) Slowly add NaOH solution (40%) to the combined filtrates (A), while stirring, until the solution is nearly neutralized. Heat on a steam bath and pour contents slowly into a 600-ml Teflon beaker containing 100 ml of hot NaOH solution (10%). Heat the solution to boiling and boil for 2 min. Allow the precipitate to settle. Place a 9-cm medium filter paper in a plastic funnel and wash the paper with 50 ml of hot NaOH solution (5%). Discard the wash solution. Filter, collecting the hot NaOH solution in a platinum dish and wash well with hot NaOH solution (5%). Reserve the filtrate and washings (B).

(f) Dissolve the precipitate on the paper with 50 ml of hot H_2SO_4 (1+5), collecting the solution in the original beaker. Wash thoroughly with hot H_2SO_4 (1+99). Nearly neutralize the solution with NaOH. Heat gently and pour into 50 ml of hot NaOH (10%) solution. Heat to boiling and boil for 2 min, allow precipitate to settle. Filter the solution through a plastic funnel containing a 9-cm filter paper. Wash well with hot NaOH solution. Combine the filtrate and washings with the reserved filtrate (B) and evaporate to a volume of about 300 ml.

(g) Neutralize the solution with HCl and add a few drops excess. Transfer to a 600-ml beaker and digest on the steam bath. Adjust the solution to pH 7 with the specially prepared NH_4OH. Digest on a steam bath for 30 min. Check the pH of the solution with a pH meter and adjust to pH 7, if necessary. Filter the precipitate through a 11-cm medium filter paper and wash 5 times with hot, neutral NH_4Cl solution (2%). Discard the filtrate and washings.

(h) Transfer the paper and contents to a 300-ml Kjeldahl flask. Slowly add 10 ml of H_2SO_4. Digest for about 15 min. Add 25 ml of HNO_3 and digest on a steam bath for 15 min. Heat over an open flame until most of the HNO_3 is expelled. Cautiously add 5 ml HNO_3 and heat to fumes

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of H_2SO_4. Continue the addition of HNO_3 and the heating until organic matter is destroyed. Cool, add 10 ml of water and evaporate until fumes of H_2SO_4 appear. Cool, add 90 ml of water, and digest on a steam bath. Filter the solution through a 9-cm fine filter paper catching the filtrate in a 600-ml beaker. Wash thoroughly with hot water. Discard the filter paper.

(i) Add 5 ml of the citric acid solution, and dilute to about 325 ml. Add 10 ml of H_2O_2 (3%), neutralize with the specially prepared NH_4OH and add 10 ml in excess. Add 5 ml of the NaCN solution and heat to 60 °C. Remove from the heat, slowly add 25 ml of 8-quinolinol solution and stir vigorously for 15 min. (Use 0.22 ml of the acetic acid solution of 8-quinolinol per mg of aluminum, plus 2 ml excess). Avoid a large excess of the 8-quinolinol solution to prevent contamination of the aluminum precipitate with reagent. Digest on top of a steam bath for 15 min. Cool the solution to room temperature and filter, using moderate suction, through a weighed 35-ml fritted glass crucible of fine porosity. Wash 8 to 10 times with the cool wash solution and 5 to 10 times with hot water. Finally wash with cold water until the washings are colorless.

(j) Dry the crucible and contents at 140 °C for 1.5 hr. Cool for 1 hr in a desiccator and weigh. Repeat, if necessary, to constant weight.

VI. Calculation

Calculate the percentage alumina as follows:

$$Al_2O_3, \text{ percent} = \frac{A \times 0.1109}{B} \times 100$$

where:

A = grams of aluminum oxyquinolinol, and

B = grams of sample used.

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ALUMINA BY THE AMMONIUM HYDROXIDE-CUPFERRON-(GRAVIMETRIC) METHOD

I. Scope

This method covers the determination of alumina in concentrations from 20 to 70 percent. The relative standard deviation is 0.36 percent.

II. Principle of Method [1]

Silicon is removed with hydrofluoric acid. An aliquot portion is treated with ammonium hydroxide and the impure Al_2O_3 is ignited and weighed. Another aliquot portion of the same volume is treated with cupferron and the precipitate is ignited and weighed. Phosphorus is determined in a third aliquot spectrophotometrically by the molybdenum blue method. The percent P_2O_5 in the sample is calculated. The weights of the oxides in the cupferron precipitate and the SiO_2 in the NH_4OH precipitate are deducted from the weight of the impure Al_2O_3. The percentages of $Al_2O_3 + P_2O_5 + Cr_2O_3$ are determined and the alumina is obtained by deducting the percents of P_2O_5 and Cr_2O_3.

III. Interferences

The amount of chromium in the NH_4OH precipitate is uncertain due to possible oxidation during solution of the sample. Any Cr_2O_3 in the precipitate may be partially oxidized during ignition. The separation of chromium may be assured by its oxidation to the sexivalent state after dissolution of the sample or it may be determined on another sample.

IV. Reagents

(a) Ammonium Hydroxide Solution. Proceed as directed in Section IV of 8-quinolinol method. See page 13.

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(b) Cupferron Solution (60g/1). Dissolve 6g of cupferron in 80 ml of cold water, dilute to 100 ml, and filter. Prepare fresh as needed.

V.   Procedure

(a) Transfer 2g of sample to a weighing bottle and dry for 2 hr at 140 °C. Stopper the bottle and cool 1 hr in a desiccator. Lift the stopper momentarily, replace, and weigh the bottle and sample. Transfer the sample, without brushing, to a 1-liter platinum dish. Reweigh the bottle.

(b) Add 25 ml of water, 15 ml of H_2SO_4, 25 ml of HNO_3, and 20 ml of HF to the covered dish and mix. Digest on a steam bath for 30 min, with occasional stirring. Remove and wash the cover. Rinse the dish thoroughly, evaporate the solution to fumes of H_2SO_4 and cool. Rinse the dish, mix, evaporate to fumes of H_2SO_4, cool and repeat this operation. Cautiously add 100 ml of warm water, and heat until the salts are in solution. Add paper pulp, and filter through a 9-cm fine filter paper into a 400-ml beaker. Wash the paper thoroughly with hot water and reserve the filtrate (A).

(c) Transfer the paper and residue to a platinum crucible and ignite at 600 °C. Cool, add 1g of Na_2CO_3, cover, and fuse over an open flame for 15 min. Cool and transfer the crucible and lid to a 250-ml Teflon beaker. Add 50 ml of water and heat on a steam bath to dissolve the fusion. Acidify the solution with H_2SO_4 (1+1) and add 1 ml excess. Remove the crucible and lid and rinse. Filter the solution through a 9-cm fine filter paper containing paper pulp and wash thoroughly with hot water. Combine the filtrate with reserved filtrate (A).

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(d) Transfer the paper and residue to a platinum crucible and ignite at 600 °C. Cool, add 2 ml of water, 5 ml of H_2SO_4 (1+1) and 5 ml of HF. Evaporate to fumes of H_2SO_4 on an air bath. Cool, rinse the crucible with water and mix. Evaporate to fumes of H_2SO_4. Cool, add 15 ml of water, and add the solution to the reserved filtrate (A).

(e) Warm a 500-ml volumetric flask at 110 °C, insert a glass tube, and remove moisture by means of a vacuum. Stopper the flask and cool to room temperature. Weigh the flask to the nearest milligram, using a second flask as a tare. Transfer the reserved filtrate (A) to the weighed flask, dilute to the mark with water, and mix. Reweigh the flask and solution, using the tare.

(f) Using a pipet, transfer 100 ml of the solution to a weighed 600-ml beaker containing a cover. Reweigh the covered beaker and solution immediately to the nearest milligram. Reserve aliquot (A) for precipitation with ammonium hydroxide.

(g) Using a pipet, transfer another 100 ml of the solution to a weighed 400-ml beaker containing a cover. Reweigh the covered beaker and solution immediately to the nearest milligram. Reserve aliquot (B) for precipitation with cupferron.

(h) Using pipets, transfer duplicate 4-ml aliquot portions of standard clay solution SRM 97A, and duplicate 15-ml aliquot portions of standard clay solution SRM 98A, to four 125-ml Erlenmeyer flasks. Reserve these aliquots (C) and (D), respectively for the determination of phosphorus spectrophotometrically.

PRECIPITATION WITH AMMONIUM HYDROXIDE
(Al_2O_3, Fe_2O_3, TiO_2, ZrO_2, P_2O_5, V_2O_5, Cr_2O_3)

(i) Dilute the reserved aliquot (A), above, to 350 ml with water and heat on a steam bath. Adjust the solution to pH 7.0 with the specially prepared NH_4OH. Heat to boiling and boil for 2 min. Allow the precipitate to settle. Check the pH of the solution, and adjust to pH 7.0, if necessary. Filter the precipitate through a 12.5 cm medium filter paper and wash 5 times with hot, neutral NH_4Cl solution (2 percent). Discard the filtrate.

(j) Transfer the paper and contents to the original beaker. Add 50 ml of hot HCl (1+1) and stir to dissolve the precipitate and to macerate the paper. Dilute to 350 ml with hot water. Adjust the solution to pH 7.0 with NH_4OH. Heat to boiling and boil for 2 min. Allow the precipitate to settle. Check the pH of the solution and filter on a medium filter paper. Do not allow the precipitate to run dry. Wash with 150 ml of hot, neutral NH_4Cl solution (2 percent), keeping the filter paper nearly filled. Drain thoroughly and transfer the paper and contents to a weighed platinum crucible.

(k) Dry and heat slowly to 600 °C, until the carbon is destroyed and finally heat at 1200 °C for 1 hr. Cover the crucible, transfer to a desiccator and weigh after 30 min. Reheat the crucible at 1200 °C for 3 min, cool in a desiccator and weigh. Reheat and reweigh, if necessary, to constant weight within 0.2 mg. The weighed precipitate contains Al_2O_3, Fe_2O_3, TiO_2, ZrO_2, P_2O_5, V_2O_5 and some Cr_2O_3.

(l) Add 4g of potassium pyrosulfate to the crucible and fuse over a low flame until a clear solution is obtained. Cool and transfer to a 150-ml beaker. Add 100 ml of H_2SO_4 (1+9) and heat on a steam bath to dissolve the melt. Remove and rinse the crucible. Evaporate the

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solution to fumes of H_2SO_4, cover and fume for 5 min. Cool, dilute to 125 ml with warm water and heat. Filter and wash well with hot water. Transfer the paper to a platinum crucible, dry and heat to 600 °C. Finally, heat the crucible at 1200 °C for 30 min. Cover the crucible, cool in a desiccator and weigh. Moisten the precipitate with 3 drops of water, add 3 drops of H_2SO_4 (1+1) and 5 ml of HF. Heat on an air bath to fumes of H_2SO_4 and continue heating to expel H_2SO_4. Ignite the crucible over an open flame for 5 min with the cover open. Cool in a desiccator for 30 min and weigh. The difference in weight is the silica in the NH_4OH precipitate.

PRECIPITATION WITH CUPFERRON (Fe_2O_3, TiO_2, ZrO_2, V_2O_5)

(m) Neutralize the reserved aliquot (B) with the specially prepared NH_4OH and then acidify with H_2SO_4 (1+1). Add 40 ml of H_2SO_4 (1+1), dilute to 175 ml with water, and stir. Cool the solution in an ice bath. Add slowly 25 ml of cold cupferron solution (6 percent) and stir. Digest in an ice bath for several min, add paper pulp and stir. Using moderate suction, filter the precipitate through a 11-cm fine filter paper supported by a platinum cone in a funnel. Wash thoroughly with chilled HCl (1+9) containing 25 ml of cupferron solution per liter. Transfer the paper and contents to a platinum crucible. Heat slowly at 600 °C until the carbon is destroyed.

(n) Cool and add 3g of $K_2S_2O_7$ and fuse over a low flame until a clear solution is obtained. Cool, transfer the crucible to 400-ml beaker and add 100 ml of H_2SO_4 (1+9). Heat to dissolve the fusion, remove and rinse the crucible. Dilute to 170 ml with H_2SO_4 (1+9) and add 5 ml of H_2SO_4 (1+1). Cool in an ice bath, add 25 ml of cold cupferron solution and add paper pulp. Filter and wash the precipitate as directed in the preceding paragraph. Transfer the paper and contents to a

weighed platinum crucible. Dry at 50 °C. Heat slowly to 600 °C until carbon is destroyed and finally heat at 1200 °C for 1 hr. Cover the crucible, transfer to a desiccator, and weigh after 30 min. Reheat the crucible at 1200 °C for 30 min, cool in a desiccator and weigh. Reheat and reweigh, if necessary, to constant weight within 0.2 mg. The weighed precipitate contains Fe_2O_3, TiO_2, and V_2O_5. Reserve the oxides for the gravimetric determination of titania.

VI. <u>Calculation</u>

See page 28.

A useful procedure for the spectrophotometric determination of phosphorus involves the phosphomolybdenum blue complex. The method is based on the measurement of the blue color which develops when a heteropoly acid formed by phosphate and molybdate is reduced with hydrazine sulfate, hydroquinone, ferrous sulfate, or sodium bisulfite. Arsenic and germanium form yellow heteropoly acids which produce a blue color on reduction. Arsenic and germanium can be volatilized by fuming with hydrochloric and hydrobromic acids.

Phosphorus can also be determined by the phosphovanadomolybdate method which is based on the formation of a yellow complex, but the molybdenum blue method is the more sensitive.

A dependable gravimetric method for phosphorus involves its precipitation as ammonium phosphomolybdate and conversion to magnesium pyrophosphate.

PHOSPHORUS BY THE MOLYBDENUM-BLUE (PHOTOMETRIC) METHOD

I.   Scope

This method covers the determination of phosphorus pentoxide in concentrations from 0.03 to 1.5 percent. The relative standard deviations at the low and high ranges are 0.002 and 0.1 percent, respectively.

II. Principle of Method [6]

Phosphorus as the ortho acid forms a blue complex with hydrazine sulfate and ammonium molybdate. Photometric measurement is made at 650 nm.

III. Interferences

Arsenic above 0.05 percent interferes and must be separated by volatilization with HBr. Germanium, if present, will be removed by treatment with HBr and HCl.

IV.   Concentration Range

The recommended concentration range is from 0.001 to 0.04 mg of phosphorus per 50 ml of solution, using a 2-cm cell.

V.   Stability of Color

The color develops within 5 min at 98 °C and is stable for at least 24 hr. Readings are usually made within 30 min.

VI.   Reagents

(a) Ammonium Molybdate Solution (2 percent in 11 $\underline{N}$ H_2SO_4). Add 300 ml of H_2SO_4 (sp gr 1.84) to 500 ml of water and cool. Dissolve 20g of ammonium molybdate in the acid and dilute to 1 liter with water.

(b) Ammonium Molybdate - Hydrazine Sulfate Solution. Dilute 25 ml of the ammonium molybdate solution to 80 ml with water, add 10 ml of the hydrazine sulfate solution, and dilute to 100 ml with water. This solution is not stable and should be prepared as needed.

(c) Hydrazine Sulfate Solution (0.15 percent). Dissolve 1.5g of hydrazine sulfate in 1000 ml of water.

(d) Phosphorus, Standard Solution (A) (1 ml $\approx$ 0.4 mg of P). Dissolve 1.8312g of Na_2HPO_4 in 200 ml of water, add 35 ml of HNO_3 (1+1), dilute to 1 liter in a volumetric flask with water and mix.

(e) Phosphorus, Standard Solution (B) (1 ml $\approx$ 0.01 mg P). Using a pipet, transfer 5.0 ml of standard phosphorus solution (A) to a 200-ml volumetric flask, dilute to the mark with water and mix. Prepare this solution fresh as needed.

(f) Sodium Sulfite Solution (10 percent). Dissolve 100g of anhydrous Na_2SO_3 in 500 ml of water and dilute to 1 liter. Filter through a fine filter paper, but do not wash.

VII. Preparation of Calibration Curve

(a) Transfer 0, 0.5, 1.0, 2.0, 3.0 and 4.0 ml aliquot portions of standard phosphorus solution (B) to six 125-ml Erlenmeyer flasks.

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(b) Add 5 ml of HNO_3 (1+1) and 3.0 ml of $HClO_4$ (60 percent). Evaporate to fumes and fume gently 3 or 4 min to remove HNO_3.

(c) Cool and add 5 ml of HBr (1+4). Evaporate to fumes and fume gently to remove HBr. Cool, rinse the flask with 5 ml of water and evaporate to fumes. Cool somewhat, and add 10 ml of water and 15 ml of Na_2SO_3 solution. Heat to boiling and boil gently for 30 sec. Add 20 ml of the ammonium molybdate-hydrazine sulfate reagent, heat to 95-98 °C and digest at this temperature for 4 to 5 min. Then heat the solution just to boiling temperature, but do not boil. Cool rapidly to room temperature and transfer the solution to a 50-ml volumetric flask. Rinse the 125-ml flask with 2-ml portions of a dilute solution of the ammonium molybdate-hydrazine sulfate reagent (1+4) and transfer the washings to the 50-ml flask. Dilute to the mark with the diluted solution of the reagent and mix.

(d) Transfer a portion of the solution to a 2-cm absorption cell and measure the transmittance or absorbance at 650 nm, using water as a reference solution for 100 percent transmittance or zero absorbance. Plot the values obtained against milligrams of phosphorus per 50 ml of solution. (Note 1, see page 11.)

VIII. Procedure

(a) Proceed as directed in Section VII, b through d (above), with reserved aliquots C and D prepared in Section V, h of method for determination of Alumina by Ammonium Hydroxide-Cupferron. See page 17.

(b) From the value obtained, determine the milligrams of phosphorus present in 50 ml of the final solution.

(c) Carry a reagent blank through the entire procedure using the same amounts of all reagents but with the sample omitted.

IX. Calculation

Calculate the percentage of phosphorus pentoxide as follows:

$$P_2O_5, \text{ percent} = \frac{(A - B) \times 2.2914}{C \times 10}$$

where:

A = milligrams of phosphorus found in 50 ml of final test solution.

B = milligrams of phosphorus found in 50 ml of the reagent blank, and

C = grams of sample in 50 ml of the final test solution.

PHOSPHORUS BY THE ION-EXCHANGE (PHOTOMETRIC) METHOD

I. Scope

This method covers the determination of phosphorus pentoxide in concentrations from 0.03 to 1.5 percent.

II. Principle of Method [6, 7, 8]

After fusion of the sample with lithium metaborate, the fusion is stirred in water containing cation exchange resin. SiO_2, B_2O_3 and P_2O_5 are eluted with water. Silica is separated with HF and phosphorus is determined spectrophotometrically.

III. Interferences

Arsenic and germanium interfere and must be separated by volatilization with HBr and HCl.

IV. Reagents

(a) Lithium Metaborate, Anhydrous, $LiBO_2$.

(b) Resin, Cation Exchange, Dowex 50W-X4 (100-200 mesh).

V. Procedure

(a) Transfer 0.5g of clay SRM 97A or 0.3g of clay SRM 98A sample to a weighing bottle and dry for 2 hr at 140 °C. Cool for 1 hr in a desiccator, and weigh the bottle and sample after opening the bottle momentarily. Transfer the sample to glazed paper and reweigh the bottle. The difference is the weight of the sample. Add 2.5g of $LiBO_2$ to the glazed paper and mix thoroughly. Transfer to a graphite crucible and fuse in a muffle furnace at 950 °C for 20 min. Remove the crucible, and transfer the fusion to a 400-ml Teflon beaker containing 100 ml of water, and stir.

(b) Decant the aqueous solution into a Teflon beaker and reserve (A). Transfer the fusion to an agate mortar, grind to a powder, and transfer to the beaker containing the water (A). Add double the milliequivalent weight of dry cation resin Dowex 50W-X4 required for the aluminum and lithium. Stir for one hr and allow to settle. Decant the solution and reserve (B). Transfer the resin to a column containing a plug of

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polyethylene wool and transfer the reserved solution (B) to the column. Adjust the flow rate to 35 to 45 drops per min. Elute with 400 ml of water and reserve the eluted solutions (C), which contain SiO_2, B_2O_3, and P_2O_5. Elute with 25 ml of water and test for the presence of silicon spectrophotometrically.

(c) Add 10 ml of $HClO_4$ to the reserved solution (C) and evaporate the solution of standard 97A to a volume of about 225 ml or the solution of standard 98A to a volume of about 90 ml. Transfer the former to a 250-ml volumetric flask or the latter to a 100-ml volumetric flask. Dilute to mark with water, and mix.

(d) Using pipets, transfer a 10-ml aliquot portion of standard 97A or a 20-ml aliquot of 98A to a platinum crucible. Add 2.6 ml or 1.0 ml of $HClO_4$ to the crucibles containing 97A and 98A, respectively. Add 10 ml of HF and evaporate to fumes in an air bath. Cool, rinse the crucible, and mix. Again evaporate to fumes of $HClO_4$. Proceed as directed in Section VII (c), (d), of the method for the determination of Phosphorus by the Molybdenum-Blue (Photometric). See page 23.

The value obtained for phosphorus is calculated as P_2O_5 and deducted from the impure Al_2O_3 precipitate obtained in the determination of alumina by the Ammonium Hydroxide-Cupferron-Gravimetric Method. See page 17.

Chromium is determined as Cr_2O_3 in a subsequent section and is also deducted from the impure Al_2O_3. See page 46.

VI. Calculation

Calculate the percentage alumina as follows:

$$E = \frac{A - (B + C)}{D} \times 100$$

Al_2O_3, (percent) $= E - (F + G)$

where:

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A = grams of oxides in the NH_4OH precipitate in 100 ml aliquot portion,

B = grams of oxides in the cupferron precipitate in 100 ml aliquot,

C = grams of silica in the NH_4OH precipitate,

D = grams of sample in 100 ml aliquot,

E = percent Al_2O_3 + P_2O_5 + Cr_2O_3,

F = percent P_2O_5, and

G = percent Cr_2O_3.

TITANIA BY CUPFERRON (GRAVIMETRIC) METHOD

I. Principle of Method [1]

After separation of silica with HF, iron, titanium,
zirconium, and vanadium are precipitated with cupferron.
The ignited oxides are fused with $K_2S_2O_7$ and dissolved in
H_2SO_4. Iron, titanium, and zirconium are separated from
vanadium by precipitation with NaOH solution. The
precipitate is dissolved in HCl. Tartaric acid is
added, and the solution is treated with H_2S. Iron, in
the filtrate, is removed as FeS by ammoniacal precip-
itation with H_2S. Titanium and zirconium are precip-
itated with cupferron and the ignited oxides are
weighed. After fusion with $K_2S_2O_7$, silica is
dehydrated, determined, and the weight of the oxides
corrected for silica. Hydrogen peroxide is added,
zirconium is precipitated with $(NH_4)_2HPO_4$ and ignited to
ZrP_2O_7 and weighed. The gravimetric value for TiO_2 is
obtained by deducting the weight of the zirconium as ZrO_2
from the combined weight of $ZrO_2 + TiO_2$.

II. Reagents

(a) Cupferron (60g/l). Dissolve 6g of cupferron in
80 ml of cold water, dilute to 100 ml, and filter. Prepare
fresh as needed.

(b) Diammonium Hydrogen Phosphate. [$(NH_4)_2HPO_4$].

(c) Hydrogen Peroxide Solution. (H_2O_2) 30 volume
percent.

(d) Hydrogen Sulfide. (H_2S).

(e) Tartaric Acid. Reagent grade.

(f) Wash Solution. Dissolve 5g of NH_4Cl in 1 liter of
water, add 15 ml of NH_4OH, and saturate with H_2S.

III. Procedure

(a) Fuse the reserved oxides of iron, titanium,
zirconium, and vanadium, Section V, (n) of the Alumina-
Cupferron-Gravimetric Method, with 3g of $K_2S_2O_7$. See page 22.

Cool and transfer the crucible to a 250-ml beaker. Add
100 ml of H_2SO_4 (1+9) and heat to dissolve the fusion. Wash
and remove the crucible and lid.

(b) Nearly neutralize the solution with NaOH solution
(20 percent). Pour slowly, with constant stirring, into
100 ml of NaOH solution (10 percent) contained in a
platinum or Teflon container. Digest for 1 hr on a steam
bath. Filter on a filter paper previously washed several
times with NaOH solution (10 percent) and wash the precip-
itate with hot water. Discard the filtrate.

(c) Dissolve the precipitate by pouring 25 ml of hot
HCl (1+2) onto the paper and wash with hot HCl (2+98). Add
5g of tartaric acid to the solution and dilute to 200 ml
with water. Neutralize with NH_4OH and then add 2 ml of HCl
per 100 ml of solution. Heat to boiling and saturate the
solution with H_2S to precipitate any platinum. Allow to cool
and filter through a fine filter paper. Wash with H_2SO_4 (1+9)
saturated with H_2S. Discard the precipitate.

(d) Add NH_4OH to the filtrate until a black precipitate
of iron sulfide forms and then add 5 ml in excess. Treat
the solution with a rapid stream of H_2S for 5 min. Digest
at about 40 °C for 30 min and then filter through a fine
filter paper. Wash with H_2S wash solution. Discard the
filter and precipitate.

(e) Evaporate the filtrate to a volume of about 155 ml
and acidify with H_2SO_4. Add 45 ml of H_2SO_4 (1+1) and chill
the solution in ice water. While stirring, add 25 ml of the
cooled cupferron solution (60g/l). Add paper pulp and
allow to settle for several mins. Insert a platinum cone in
a funnel and filter the solution on a fine filter paper using
gentle suction. Wash thoroughly with cool HCl (1+9)
containing 25 ml of the cupferron solution.

(f) Transfer the paper to a weighed platinum crucible,
cautiously char and heat at 1200 °C for 15 min. Cool and

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weigh as $ZrO_2 + TiO_2$. Repeat the heating and weighing to constant weight.

(g) To correct for small amounts of silica in the weighed oxides, fuse the oxides with 1g of $K_2S_2O_7$. Dissolve the fusion in 50 ml of H_2SO_4 (1+9) and evaporate the solution to fumes of H_2SO_4. Cool, add 45 ml of water, and heat until salts have dissolved. Filter immediately through a 9-cm fine filter paper and wash with hot H_2SO_4 (1+9). Reserve the filtrate (A) and washings for the precipitation of zirconium. Transfer the paper and contents to a platinum crucible, char the paper, and ignite the crucible at 1200 °C for 10 min. Cool and weigh. Add several drops of H_2SO_4 (1+1), 5 ml of HF (48 percent) and evaporate to dryness on an air bath. Ignite at 1000 °C for 5 min, cool and weigh. The difference in weight is the weight of the silica in the oxides.

(h) Add 2 ml of H_2O_2 (30 percent) to the reserved filtrate (A) to oxidize titanium. Add 0.5g of $(NH_4)_2HPO_4$ to precipitate zirconium. Stir and digest overnight at about 40 °C. Filter on a 9-cm fine filter paper containing paper pulp and wash with cold NH_4NO_3 solution (5 percent). Transfer the paper to a platinum crucible, and ignite at 1050 °C. Cool, and fuse with 1g of $K_2S_2O_7$. Transfer the crucible and fusion to a 250 ml beaker. Dissolve the fusion in 50 ml of H_2SO_4 (1+9). Remove and rinse the crucible with H_2SO_4 (1+9). Add 2 ml of H_2O_2 (30 percent) and precipitate the zirconium as before. Transfer the paper to a weighed platinum crucible and ignite at 1050 °C for 15 min. Cool and weigh the zirconium as ZrP_2O_7.

IV. Calculation

Calculate the percentage titania as follows:

$$TiO_2, \text{ percent} = \frac{A - (B + C)}{D} \times 100$$

where:

A = grams of mixed oxides, $TiO_2 + ZrO_2 + SiO_2$,

B = grams of silica in the oxides,

C = grams of ZrO_2, or g of ZrP_2O_7 found X 0.4647, and

D = grams of sample used.

TITANIA BY THE HYDROGEN PEROXIDE (PHOTOMETRIC) METHOD

I. Scope

This method covers the determination of titania in concentrations from 0.02 to 0.8 percent.

II. Principle of Method [9]

After separation of silica, hydrogen peroxide is added to form a yellow complex with titanium in a sulfuric acid solution. Spectrophotometric measurement is made at 410 nm.

III. Concentration Range

The recommended concentration range is from 0.15 to 3.0 mg of titanium per 100 ml of solution, using a 2-cm cell.

IV. Stability of Color

The color is stable for at least 1 hr.

V. Interferences

Interference from vanadium is negligible because of the low concentration present in clays. Fluoride is reduced to a noninterfering level by fuming with sulfuric acid.

VI. Reagents

(a) Hydrogen Peroxide Solution (H_2O_2)-30 volume percent.

(b) Titanium, Standard Solution (A) (1 ml $\simeq$ 1.0 mg Ti). Dry 1g of NBS SRM 154a, Titanium Oxide, at 105 °C for 2 hr and cool. Transfer 0.8374g of the dried sample to a 250 ml Erlenmeyer flask. Add 10g of $(NH_4)_2SO_4$ and 25 ml of H_2SO_4. Insert a short-stemmed glass funnel in the neck of the flask and heat cautiously to boiling while rotating the flask over an open flame. Continue the heating until solution is complete. Cool and rapidly pour the solution into 400 ml of cool water, while stirring. Rinse the flask 5 times with 10 ml portions of H_2SO_4 (1+1), and transfer to a 500-ml volumetric flask. Dilute to volume with H_2SO_4 (1+9), and mix.

(c) Titanium, Standard Solution (B) (1 ml $\simeq$ 0.1 mg Ti). Using a pipet, transfer 20 ml of Solution (A) (1 ml $\simeq$ 1.0 mg

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Ti) to a 200-ml volumetric flask, dilute to volume with H_2SO_4 (1+9), and mix.

VII. Preparation of Calibration Curve

(a) Calibration Solutions. Using pipets, transfer 5, 10, 20, 25 and 30 ml of Solution (B) (1 ml ≃ 0.1 mg Ti) to 100-ml volumetric flasks. Add 90 ml of H_2SO_4 (1+9) and 4 drops of H_2O_2 (30 percent). Dilute to volume with H_2SO_4 (1+9), and mix.

(b) Reference Solution

Transfer 90 ml of H_2SO_4 (1+9) to a 100-ml volumetric flask, add 5 drops of H_2O_2 (30 percent), dilute to volume with H_2SO_4 (1+9), and mix. Using this solution, adjust the spectrophotometer to the initial setting, using a light band centered at 410 nm. While maintaining this photometric adjustment, take the photometric readings of the calibration solutions using a 2-cm cell. Plot the photometric readings of the calibration solutions against milligrams of titanium per 100 ml of solution.

VIII. Procedure

(a) Transfer 2g of sample to a weighing bottle and dry for 2 hrs at 140 °C. Transfer the sample to a platinum dish containing a cover. Add 25 ml of water, 15 ml of H_2SO_4, 25 ml of HNO_3 and 25 ml of HF and heat gently to dissolve the sample. After dissolution, heat to fumes of H_2SO_4. Cool, and cautiously add 100 ml of water. Transfer to a 500 ml volumetric flask, dilute to volume with water, and mix.

(b) Using a pipet, transfer a 50-ml aliquot to a 100 ml volumetric flask. Add 15 ml of H_2SO_4 (1+1), dilute to volume with water, and mix.

(c) Transfer a portion of the solution to a 2-cm cell and adjust the spectrophotometer to the initial setting using a light band centered at 410 nm.

(d) Add 4 drops of H_2O_2 (30 percent) to the solution remaining in the flask, mix thoroughly, and measure the absorbance or transmittance at 410 nm.

(e) From the calibration curve determine the number of milligrams of titanium per 100 ml of solution.

IX. Calculation

Calculate the percentage of titania as follows:

$$TiO_2, \text{ percent} = \frac{A \times 1.668}{B \times 10}$$

where:

A = milligrams of titanium in 100 ml of the final solution, and

B = grams of sample in 100 ml of the final solution.

IRON BY THE 1, 10-PHENANTHROLINE (PHOTOMETRIC) METHOD

I. Scope

   This method covers the determination of iron oxide in concentrations from 0.03 to 4 percent.

II. Principle of Method [10]

   The sample is dissolved in mixed acids and fumed to remove silica and HF. The pH is adjusted to 5.5-6.0, and 1,10-phenanthroline is added to form an orange-red complex with ferrous iron. Spectrophotometric measurement is made at 510 nm.

III. Interferences

   Copper, nickel and zinc form complexes and consume 1,10-phenanthroline; however, sufficient reagent is added to complex the maximum amounts of these elements, in addition to the iron.

IV. Concentration Range

   The recommended concentration range is 10 to 150 µg of iron per 100 ml of solution, using a 2-cm cell.

V. Stability of Color

   The color is stable for at least 2 hr.

VI. Reagents

   (a) Citric Acid Solution (500g/l). Dissolve 250g of citric acid in 300 ml of water and dilute to 500 ml with water.

   (b) Hydroxylamine Hydrochloride Solution (100g/l). Dissolve 10g of hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in 80 ml of water and dilute to 100 ml. Prepare fresh as needed.

   (c) Iron, Standard Solution (A) (1 ml = 0.30 mg Fe). Dissolve 150.4 mg of iron (NBS Standard 55E) in 50 ml of HCl (1+1). Heat gently to dissolve the iron. Cool, transfer to a 500-ml volumetric flask, dilute to volume with water, and mix.

   (d) Iron, Standard Solution (B) (1 ml = 0.015 mg Fe). Using a pipet, transfer a 25 ml aliquot of iron solution (A) to a 500-ml volumetric flask, dilute to volume with water, and mix.

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(e) 1, 10-Phenanthroline Solution (5g/l). Dissolve 0.5g of 1,10-phenanthroline in 80 ml of hot water and dilute to 100 ml with water. Prepare fresh as needed.

(f) Sodium Acetate Solution (400g/l). Dissolve 400g of sodium acetate ($NaC_2H_3O_2 \cdot 3H_2O$) in 600 ml of water. Dilute to 1 liter.

VII. Preparation of Calibration Curve

(a) Calibration Solutions.

(1) Transfer 0.0, 1, 3, 5 and 10 ml of iron solution (B) (1 ml $\approx$ 0.015 mg Fe) to six 150-ml beakers. Add 5 ml of citric acid solution and dilute to 50 ml with water.

(2) Add successively 2 ml of the 1,10-phenanthroline solution, 2 ml of the hydroxylamine hydrochloride solution, and 10 ml of the sodium acetate solution, mixing after each addition. Adjust the pH to 5.5-6.0 with NH_4OH (1+3). Transfer the solution to a 100-ml volumetric flask, dilute to approximately 95 ml with water and mix. Place the flask in a water bath at about 70 °C for 30 min. Remove from the bath, cool to room temperature, dilute to volume with water, and mix.

(b) Spectrophotometry. Fill the reference cell with water and adjust the spectrophotometer to the initial setting using a light band centered at approximately 515 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions using a 2-cm cell.

(c) Calibration Curve. Plot the net photometric readings of the calibration solutions against milligrams of iron per 100 ml of solution.

VIII. Procedure

(a) Using pipets, transfer a 10 ml aliquot from 500 ml solution of SRM 97A, or a 4 ml aliquot from 500 ml solution of SRM 98A prepared in Section VIII (a), of Titania by the Hydrogen Peroxide (Photometric) Method to a 150-ml beaker. See page 35. Add 5 ml of citric acid

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solution and dilute to about 50 ml. Proceed as directed in Section VII (a) 2 and (b).

(b) From the value obtained, read from the calibration curve the number of milligrams of iron present in 100 ml of solution.

(c) Determine the blank correction by following the same procedure and using the same amounts of all reagents, with the sample omitted.

IX. Calculation

Calculate the percentage of iron oxide as follows:

$$Fe_2O_3, \text{ percent} = \frac{(A - B) \text{ X } 1.4298}{C \text{ X } 10}$$

where:

A = milligrams of iron in 100 ml of the final solution,

B = milligrams of iron in 100 ml of the blank, and

C = grams of sample in 100 ml of the final solution.

IRON BY $SnCl_2$ - $K_2Cr_2O_7$ (VOLUMETRIC) METHOD

I.   Scope

    This method covers the determination of iron oxide
in concentrations from 0.03 to 4 percent.

II.   Principle of Method [11]

    The sample is fused with lithium metaborate and
leached in hydrochloric acid. Iron is reduced with $SnCl_2$
and titrated with a standard solution of $K_2Cr_2O_7$.

III. Interferences

    None of the elements present interfere.

IV.   Apparatus

    Graphite crucible (1 in. X 2.5 in.)

V.   Reagents

    (a) Mercuric Chloride Solution (saturated). Dissolve
80g of $HgCl_2$ in 1 liter of hot water, stir and cool to
room temperature.

    (b) Potassium Dichromate, Standard Solution (0.01$\underline{N}$
or 1 ml ≈ 0.5585 mg Fe). Dissolve 0.4904g of $K_2Cr_2O_7$
(SRM 136c), in about 800 ml of water in a 1-liter
volumetric flask. Dilute to volume and mix. This is
a primary standard and the theoretical titer of
the solution can be used or it may be standardized
against high purity iron.

    (c) Potassium Permanganate Solution (approximately
0.1$\underline{N}$). Dissolve 0.32g of potassium permanganate ($KMnO_4$)
in 100 ml of water.

    (d) Sodium Diphenylamine Sulfonate Indicator Solu-
tion (2g/l). Dissolve 0.20g of sodium diphenylamine
sulfonate in 100 of water.

    (e) Stannous Chloride Solution (50g/l). Dissolve 5g
of $SnCl_2 \cdot 2H_2O$ in 10 ml of HCl and dilute to 100 ml with
water.

    (f) Sulfuric-Phosphoric Acid Mixture. Slowly add
150 ml of H_2SO_4 to 500 ml of water, while stirring,

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and cool to room temperature. Add 150 ml of H_3PO_4 to the cool solution, dilute to 1 liter with water, and mix.

VI. Procedure

(a) Transfer approximately 0.25g of sample to a weighing bottle and dry for 2 hr at 140 °C. Stopper the bottle and cool 1 hr in a desiccator. Lift the stopper momentarily, replace, and weigh the bottle and sample. Transfer the sample, without brushing, to a larger weighing bottle containing 1.25g of lithium metaborate and weigh the empty bottle.

(b) Mix the sample and lithium metaborate for 10 min. Transfer to a graphite crucible. Dry wash the bottle with a small portion of lithium metaborate and transfer to the crucible. Heat the crucible and contents in an electric muffle furnace at 950 °C for 15 min. While stirring, pour the hot fusion into 30 ml of HCl (1+3) in a 250-ml beaker. Cover the beaker and heat until the fusion is dissolved.

(c) Cool and add 0.1N KMnO$_4$ solution dropwise until a distinct pink color appears. Heat to boiling, boil for 1 min to expel chlorine, add $SnCl_2$ solution, drop by drop and with stirring, until the yellow color of ferric chloride disappears. Add one drop in excess, but no more. Wash the wall of the beaker and quickly cool the solution in an ice bath. Add at one stroke 10 ml of the saturated solution of mercuric chloride, stir, and wash the wall of the beaker with cool water. Allow to stand 2 to 5 min, with occasional stirring. Add 100 ml of cool water, 20 ml of H_2SO_4-H_3PO_4 mixture, and 5 drops of sodium diphenylamine sulfonate indicator. While stirring, titrate the iron with standard $K_2Cr_2O_7$ solution to a permanent reddish-violet color that persists for 1 min.

(d) Make a blank determination, following the same procedure and using the same amounts of all reagents.

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VII. Calculation

Calculate the percentage of iron oxide as follows:

$$Fe_2O_3, \text{ percent} = \frac{(A - B) \text{ C X } 0.05585 \text{ X } 1.4298}{D} \text{ X } 100$$

where:

A = milliliters of $K_2Cr_2O_7$ solution required to titrate the sample,

B = milliliters of $K_2Cr_2O_7$ solution required to titrate the blank,

C = normality of the $K_2Cr_2O_7$ solution, and

D = grams of sample used.

ZIRCONIA BY THE PYROCATECHOL VIOLET (PHOTOMETRIC) METHOD

I.   Scope

This method covers the determination of zirconium in concentrations from 0.005 to 0.5 percent.

II. Principle of Method [12, 13, 14]

Zirconium is extracted with trioctylphosphine oxide (TOPO), dissolved in cyclohexane, and forms a green complex with pyrocatechol violet which is dissolved in absolute alcohol. The photometric measurement is made at 655 nm.

III. Concentration Range

The recommended concentration range is from 4 to 40 µg of zirconium per 25 ml of solution, using a 2 cm cell.

IV. Stability of Color

The color tends to fade on standing. Photometric measurements should be made within 30 min after the addition of the pyrocatechol violet solution.

V.   Interferences

Iron and titanium interfere but are removed by back-washing the TOPO extract with HNO_3.

VI. Reagents

(a) Pyrocatechol Violet Solution. Dissolve 10 mg of pyrocatechol violet in 20 ml of absolute ethyl alcohol.

(b) Trioctylphosphine Oxide (TOPO) (0.1 Molar). Dissolve 3.86g of TOPO in 100 ml of cyclohexane.

(c) Zirconium Perchlorate, Standard Solution (A) (1 ml ≃ 1.0 mg Zr). Transfer 1.767g of $ZrOCl_2 \cdot 8H_2O$ to a 300-ml Kjeldahl flask and dissolve in 25 ml of water. Add 40 ml of $HClO_4$ and evaporate to heavy fumes. Cool, add 100 ml of water, and mix. Transfer to a 500 ml volumetric flask, dilute to volume with water, and mix.

(d) Zirconium Perchlorate, Standard Solution (B) (1 ml ≃ 4 µg Zr). Transfer a 2.0 ml aliquot of zirconium solution (A) to a 500-ml volumetric flask, and add 40 ml of

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$HClO_4$. Dilute to volume with water and mix. Prepare fresh as needed.

VII. Preparation of Calibration Curve

(a) Transfer 0.0, 1, 2, 5, and 10-ml of zirconium solution (B) (1 ml $\simeq$ 4 μg Zr) to five 60 ml separatory funnels.

(b) Dilute to 25 ml with HNO_3 (1+1). Add 5 ml of 0.1$\underline{M}$ TOPO solution, stopper the funnel, and shake for 15 min on a mechanical shaker. Allow the layers to separate and discard the lower acid layer. Add 25 ml of HNO_3 (1+1) and shake for 15 min. Allow the layers to separate and discard the acid layer.

(c) Using a pipet, transfer 2 ml of the TOPO extract to a dry 25-ml volumetric flask. Add 10 ml of absolute alcohol, and 1.5 ml of the pyrocatechol violet solution. Add 5 ml of pyridine to neutralize any acid in the TOPO extract. Dilute to volume with absolute alcohol, and mix.

(d) Fill the reference cell with water and adjust the spectrophotometer to the initial setting using a light band centered at 655 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions in a 2-cm cell within 30 min after addition of the pyrocatechol violet solution.

(e) Plot the photometric readings of the calibration solutions against micrograms of zirconium per 25 ml of solution.

VIII. Procedure

(a) Transfer 0.1g of sample to a weighing bottle and dry for 2 hrs at 140 °C. Cool, and weigh. Mix with 0.5g of anhydrous lithium metaborate and transfer the mixture to a graphite crucible. Heat the crucible and contents in an electric muffle furnace at 950 °C for 15 min. Swirl the melt and transfer to a 400-ml beaker containing 50 ml of

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HNO_3 (1+19), while stirring. Transfer the solution to a
100 ml volumetric flask and wash with 47.5 ml of HNO_3
(sp gr 1.42). Dilute to volume with water, and mix.

(b) Using a pipet, transfer a 20-ml aliquot of the
solution to a 60 ml separatory funnel and proceed as
directed in Section VII, (b) through (d).

(c) From the value obtained, determine the micrograms
of zirconium present in 25 ml of solution.

IX. Calculation

Calculate the percentage of zirconia as follows:

$$ZrO_2, \text{ percent} = \frac{A \times 1.35}{B \times 10^4}$$

where:

A = micrograms of zirconium in 25 ml of the final
test solution,

B = grams of sample in 25 ml of the final test
solution.

CHROMIUM OXIDE BY THE DIPHENYLCARBAZIDE (PHOTOMETRIC)
METHOD

I.   Scope

This method covers the determination of chromium oxide
in the range of 0.02 to 0.5 percent. The relative standard
deviation is 2 percent.

II.   Principle of Method [15]

Chromium is oxidized to the sexivalent state with
ammonium peroxydisulfate and silver nitrate. A red-violet
complex is then formed with diphenylcarbazide. The photo-
metric measurement is made at 540 nm.

III.   Interferences

Iron interferes, but is removed with NaOH. Vanadium
in amounts present in clays does not interfere if the
solution is allowed to stand for 10 to 15 min after addition
of diphenylcarbazide.

IV.   Stability of Color

The chromium diphenylcarbazide complex develops almost
immediately, but may fade after a short time. Spectrophoto-
metric measurement should be made within 15 to 30 min after
addition of diphenylcarbazide.

V.   Concentration Range

The recommended concentration range is 0.004 to 0.06 mg
of chromium in 100 ml of solution, using a 2-cm cell.

VI.   Reagents

(a) Ammonium Peroxydisulfate Solution (100g/l).
Dissolve 10g of ammonium peroxydisulfate [$(NH_4)_2S_2O_8$] in
90 ml of water. Prepare fresh as needed.

(b) Diphenylcarbazide Solution (0.32 percent). Dissolve
0.320g in 50 ml of ethyl acetate. Transfer the solution
to a 100-ml volumetric flask, dilute to volume with ethyl
acetate, and mix. Prepare fresh as needed.

(c) Potassium Dichromate, Standard Solution (A)
(1 ml $\simeq$ 1 mg Cr). Dissolve 2.829g of $K_2Cr_2O_7$ (NBS

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Standard 136c) in 500 ml of water contained in a 1-liter volumetric flask. Dilute to volume with water, and mix.

(d) Potassium Dichromate, Standard Solution (B) (1 ml $\approx$ 0.005 mg Cr). Using a pipet, transfer a 10-ml aliquot of chromium solution (A) to a 2-liter volumetric flask, dilute to volume with water, and mix.

(e) Silver Nitrate Solution (2.5g/l). Dissolve 1.25g of $AgNO_3$ in 500 ml of water.

(f) Sodium Hydroxide Solution (100g/l). Dissolve 50g of NaOH in 250 ml of water, cool, and dilute to 500 ml.

VII. Preparation of Calibration Curve

(a) Transfer 0.0, 1, 3, 5, 7, and 10 ml of chromium solution (B) (1 ml $\approx$ 0.005 mg Cr) to six 250-ml beakers and add 4 ml of H_2SO_4 (1+1).

(b) Dilute to about 50 ml with water. Add 10 ml of $AgNO_3$ solution and heat to boiling. Add 5 ml of ammonium peroxydisulfate solution and boil for 25 min. Cool rapidly and transfer to a 100-ml volumetric flask. Dilute to about 90 ml with water and add 2 ml of diphenyl-carbazide solution. Dilute to volume with water, and mix.

(c) Fill the reference cell with water and adjust the spectrophotometer to the initial setting using a light band centered at 540 nm. While maintaining this adjustment, take the photometric readings of the cali-bration solutions in a 2-cm cell within 15 to 30 min after addition of the diphenylcarbazide solution.

(d) Plot the photometric readings of the calibration solutions against milligrams of chromium per 100 ml of solution.

VIII. Procedure

(a) Transfer slowly and with stirring, a 50-ml aliquot from the 500 ml master solution prepared in Section VIII (a) of the Titania by the Hydrogen-Peroxide (Photometric) Method, see page 35, to 150 ml of NaOH

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solution (10 percent) contained in a Teflon beaker or platinum dish. Digest on a steam bath for 1 hr and heat to boiling. Allow the precipitate to settle, and filter through a 11-cm medium filter paper previously washed with NaOH (10 percent). Wash the paper and precipitate 5 times with hot water. Using litmus paper as the indicator, acidify the filtrate with H_2SO_4 (1+1) and add 20 ml in excess. Evaporate the solution to about 80 ml, cool and transfer to a 100-ml volumetric flask. Dilute to volume with water, and mix.

(b) Using a pipet, transfer a 20-ml aliquot of the solution to a 250-ml beaker and proceed as directed in Section VII (b) and (c).

(c) From the value obtained, determine the milligrams of chromium present in 100 ml of solution.

(d) Determine the blank correction by following the same procedure and using the same amounts of all reagents, but with the sample omitted.

IX. Calculation

Calculate the percentage of chromium oxide as follows:

$$Cr_2O_3, \text{ percent} = \frac{(A - B) \ X \ 1.4616}{C \ X \ 10}$$

where:

A = milligrams of chromium in 100 ml of the final test solution,

B = milligrams of chromium in 100 ml of the blank, and

C = grams of sample in 100 ml of the final test solution.

ATOMIC ABSORPTION AND FLAME EMISSION SPECTROMETRY

The use of atomic absorption and flame emission
spectrometry as analytical techniques are firmly established.
Their applications to the determination of the alkali metals
such as lithium, sodium and potassium and to the determi-
nation of the alkaline-earth metals such as magnesium,
calcium, strontium and barium, all important constituents
of clay materials, are simple, rapid and reliable.

This section presents practical and well-established
spectrometric methods for the analyst and includes a
procedure for dissolution of the sample, interferences,
reagents, preparation of calibration curves, and clear
stepwise directions for performing the analyses.

The instrumental system used in this work is outlined
and described in detail.

INSTRUMENTATION

The instrumental system used in this work consists of the following eight basic units, (1) a 0.5m monochromator with exchangeable gratings having 1180 grooves per mm blazed for 3000 and 7500 Å and a dispersion of 1.6 Å per mm of slit width, (2) adjustable flame housing with a total consumption nebulizer burner with O_2 - H_2 gases or premixed air-acetylene and nitrous oxide-acetylene burner, (3) gas flow meters and pressure regulators, (4) multiplier phototube (EMI 9558 AQ7), (5) 0 to 2100 V multiplier phototube power supply, (6) selective amplifier and synchronous detector, (7) recorder, and (8) digital readout.

The atomic absorption instrument is similar to the flame emission equipment except that the mechanical chopper is placed between the hollow-cathode lamp and the nebulizer burner.

PROCEDURE FOR DISSOLUTION OF CLAY MATERIALS FOR FLAME
EMISSION AND ATOMIC ABSORPTION ANALYSES

1. Transfer 0.2g of sample, dried for 2 hr at 140 °C, to a Teflon-lined pressure container [16].

2. Add 1 drop each of HCl and HNO_3 and 4 ml of HF.

3. Seal the container and place in an oven at 125 °C for 2 hrs.

4. Remove from the oven, cool, open the container and transfer the solution, to a platinum dish.

5. Add 5 ml of HF and 5 ml of $HClO_4$.

6. Heat on a hot plate to dense fumes of $HClO_4$.

7. Cool, add 1 ml of HCl and 10 ml of H_2O.

8. Warm the sample to dissolve the salts.

9. Cool and transfer the solution to a 25-ml volumetric flask, dilute to volume and mix.

10. Transfer the solution to a plastic bottle for subsequent use.

I. Scope

This flame emission method is applicable to the determination of 0.2 to 1 µg of lithium per milliliter of solution in clay materials. In this range, the relative standard deviation of the method is 1 percent.

II. Principle of Method

Lithium is excited to emission in an oxygen-hydrogen flame and is then determined by measuring the radiation intensity of the light emitted at a wavelength of 6708 Å.

III. Interferences

The resonance line of lithium at 6708 Å is relatively free of spectral line interferences. However, elements such as sodium, calcium and strontium produce a continuum or unresolved band structure in this region of the spectrum. The CaO-CaOH and SrOH bands may cause an increase in flame background. The magnitude of this interference will depend upon the resolution of the monochromator. To make the appropriate background correction it is necessary to scan the wavelength region of the lithium line.

IV. Reagents

(a) Lithium, Standard Solution A (1 ml ≃ 1.000 mg Li). Dry approximately 1 gram of reagent grade Li_2CO_3 at 110 °C for 2 hours. Cool in a desiccator. Transfer 0.5324 + 0.0002g of the dry Li_2CO_3 to a 100-ml volumetric flask. Add 60 ml of water and 3 ml of HCl to dissolve the Li_2CO_3. Swirl the solution to expel CO_2, dilute to volume with water, and mix.

(b) Lithium, Standard Solution B (1 ml ≃ 20 µg Li). Using a pipet, transfer 2 ml of Solution A (1 ml ≃ 1.000 mg Li) to a 100-ml volumetric flask, dilute to volume with water, and mix.

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V. Preparation of Calibration Curve

1. Using pipets, transfer 1, 2, 3, 4 and 5 ml of Solution B (1 ml ≈ 20 μg Li) to 100 ml volumetric flasks, dilute to volume with water, and mix.

2. Turn on the operating switches of the flame emission spectrometer.

3. Set the voltage to the multiplier phototube at 1000 v.

4. Install the total consumption burner in the flame housing.

5. Open the valves to the oxidant (oxygen) and fuel (hydrogen) cylinders and set the tank regulators at 30 and 20 psi, respectively.

6. Ignite the burner and adjust the pressure and/or flow rates recommended by the manufacturer.

7. Set the wavelength dial of the monochromator to 6807 $\overset{\circ}{A}$ and the slit width at 50 μ .

8. Aspirate the lithium solution with the highest concentration (1 ml ≈ 1 μg Li) from the series prepared in Step 1.

9. Adjust the gain of the operational amplifier to give 85 percent of full scale, as indicated on the recorder.

10. While aspirating, set the wavelength dial of the monochromator at 6804 $\overset{\circ}{A}$ and scan the lithium line at 6807 $\overset{\circ}{A}$ at a rate of 10 $\overset{\circ}{A}$/min.

11. Repeat step 10 with each calibration solution, in turn, and record its radiation intensity. Aspirate water between each standard solution and record the radiation intensity.

12. Plot the radiation intensity values, corrected for background, against micrograms of lithium per milliliter on rectangular coordinate paper.

VI.   Procedure

1.   Transfer to two 25-ml volumetric flasks, A and B, two equal test portions containing 10 to 15 µg of lithium.

2.   Dilute test portion A to volume with water and mix.

3.   To test portion B, add 5 µg of lithium, dilute to volume with water, and mix.

4.   Aspirate test portions A and B, and measure the radiation intensity of each. Aspirate water after each test portion.

5.   From the calibration curve, determine the lithium concentration as µg/ml.

6.   Subtract the concentration, µg/ml, that was added to test portion B. If the concentrations of the two test portions agree, proceed to step 7. If the recoveries do not agree, correct by the standard addition method (Note 1) and proceed to step 7.

7.   Calculate the percent lithium as follows:

$$\text{Li}_2\text{O, weight percent} = \frac{C \times Z \times 2.1528}{W \times 10^4}$$

where:

C = lithium concentration, µg/ml

Z = dilution factor

W = test portion of solid sample, grams.

Note 1 - See, Menis, O. and Rains, T. C. Sensitivity, Detection Limits, Precision and Accuracy in Flame Emission and Atomic Absorption Spectrometry. Chapter II pp 47-77 in Analytical Flame Spectroscopy—Selected Topics.
Radu Mavrodineanu, Editor. MacMillan and Co. Ltd. (1970), New York.

SODIUM BY FLAME EMISSION SPECTROMETRY

I. Scope

This flame emission method is applicable to the determination of 1 to 5 µg of sodium per milliliter of solution in clay materials. In this range, the relative standard deviation of the method is 1 percent.

II. Principle of Method

Sodium is excited to emission in an oxygen-hydrogen flame and is then determined by measuring the radiation intensity of the light emitted at a wavelength of 5890 $\overset{\circ}{A}$.

III. Interferences

The resonance line of sodium at 5890 $\overset{\circ}{A}$ shows very little spectral interference from other elements. Because of the high sensitivity of sodium emission, the flame background, due to a continuum or unresolved band structure, is very small when the resolution of the monochromator is better than 1 $\overset{\circ}{A}$. The major sources of errors are from the contamination of sodium during the preparation of the sample, and from air-borne dust particles during the flame emission measurements. Extreme care must be taken in handling the sample and disposable or clean gloves must be worn at all times.

IV. Reagents

(a) Sodium, Standard Solution A (1 ml ≃ 10.0 mg Na).
Dry approximately 5 grams of reagent grade NaCl at 110 °C for 2 hrs. Cool in a desiccator. Transfer 2.542 $\pm$ 0.001g of the dry NaCl to a 100-ml volumetric flask, dissolve in 50 ml of water and then add 10 ml of ultra pure 1$\underline{N}$ HCl. Dilute to volume with water, and mix.

(b) Sodium, Standard Solution B (1 ml ≃ 100 µg Na).
Using a pipet, transfer 1 ml of Solution A (1 ml ≃ 10.0 mg Na) to a 100-ml volumetric flask, dilute to volume with water, and mix.

V.   Preparation of Calibration Curve

1.   Using pipets, transfer 1, 2, 3, 4 and 5 ml of
Solution B (1 ml ≃ 100 μg Na) to 100-ml volumetric flasks,
dilute to volume with water, and mix.

2-6.   Proceed as directed in steps 2 to 6 of Section V
of the procedure for lithium. See page 53.

7.   Set the wavelength dial of the monochromator to
5890 Å and slit width at 50 μ

8.   Aspirate the sodium solution with the highest
concentration (1 ml ≃ 5 μg Na) from the series prepared
in Step 1.

9.   Adjust the gain of the operational amplifier
to give 85 percent of full scale, as indicated on the
recorder.

10.   While aspirating, set the wavelength dial of the
monochromator at 5885 Å and scan the sodium line at 5890 Å
at a rate of 10 Å/min.

11.   Repeat step 10 with each calibration solution,
in turn, and record the radiation intensity. Aspirate water
between each standard solution and record the radiation
intensity.

12.   Plot data as directed in step 12 of the procedure
for lithium. See page 53.

VI.   Procedure

1.   Transfer to two 25-ml volumetric flasks, A and B,
two equal test portions containing 25 to 50 μg of sodium.

2.   Dilute test portion A to volume with water and
mix.

3.   To test portion B, add 25 μg of sodium, dilute
to volume with water and mix.

4-6.   Proceed as directed in steps 4 to 6 of Section VI
of the procedure for lithium. See page 54.

7.   Calculate the percent sodium as follows:

$$Na_2O, \text{ weight percent} = \frac{C \times Z \times 1.348}{W \times 10^4}$$

where:

C = sodium concentration, $\mu g/ml$

Z = dilution factor

W = test portion of solid sample, grams.

POTASSIUM BY FLAME EMISSION SPECTROMETRY

I. Scope

This flame emission method is applicable to the determination of 2 to 10 µg of potassium per milliliter of solution in clay materials. In this range, the relative standard deviation of the method is 1 percent.

II. Principle of Method

Potassium is excited to emission in an oxygen-hydrogen flame and is then determined by measuring the radiation intensity of the light emitted at a wavelength of 7665 $\overset{\circ}{A}$.

III. Interferences

The potassium doublet at 7665 and 7699 $\overset{\circ}{A}$ suffers seriously from the spectral interference of rubidium which emits strongly at 7800 $\overset{\circ}{A}$. To overcome this interference, it is necessary to have an instrument with good dispersion and resolution. Another source of interference results from the enhancement of the emission of potassium when rubidium or cesium are present. This is due to the repression of the ionization of potassium by electrons produced by these elements in the flame. This enhancement can be corrected by means of the standard addition method.

IV. Reagents

(a) Potassium Standard Solution A (1 ml $\simeq$ 10.0 mg K). Dry approximately 2 grams of reagent grade KCl at 110 °C for 2 hrs. Cool in a desiccator. Transfer 1.907 $\pm$ 0.001g of the dry KCl to a 100-ml volumetric flask, dissolve in 50 ml of water and then add 10 ml of ultra pure 1$\underline{N}$ HCl. Dilute to volume with water, and mix.

(b) Potassium, Standard Solution B (1 ml $\simeq$ 100 µg K). Using a pipet, transfer 1 ml of Solution A (1 ml $\simeq$ 10.0 mg K) to a 100-ml volumetric flask, dilute to volume with water, and mix.

V. Preparation of Calibration Curve

1. Using pipets, transfer 2, 4, 6, 8 and 10 ml of Solution B (1 ml ≃ 100 µg K) to 100 ml volumetric flasks, dilute to volume with water and mix.

2-6. Proceed as directed in steps 2 to 6 of Section V of the procedure for lithium. See page 53.

7. Set the wavelength dial of the monochromator to 7665 Å and the slit width at 50 µ.

8. Aspirate the potassium solution with the highest concentration (1 ml ≃ 10 µg K) from the series prepared in Step 1.

9. Adjust the gain of the operational amplifier to give 85 percent of full scale, as indicated on the recorder.

10. While aspirating, set the wavelength dial of the monochromator at 7660 Å and scan the potassium line at 7665 Å at a rate of 10 Å/min.

11. Repeat step 10 with each calibration solution, in turn, and record its radiation intensity. Aspirate water between each standard solution and record the radiation intensity.

12. Plot data as directed in step 12 of the procedure for lithium. See page 53.

VI. Procedure

1. Transfer to two 25-ml volumetric flasks, A and B, two equal test portions containing 50 to 100 µg of potassium.

2. Dilute test portion A to volume with water and mix.

3. To test portion B, add 50 µg of potassium, dilute to volume with water and mix.

4-6. Proceed as directed in steps 4 to 6 of Section VI of the procedure for lithium. See page 54.

7. Calculate the percent potassium as follows:

$$K_2O, \text{ weight percent} = \frac{C \times Z \times 1.205}{W \times 10^4}$$

where:

C = potassium concentration, µg/ml

Z = dilution factor

W = test portion of solid sample, gram.

I. Scope

This atomic absorption method is applicable to the determination of 0.4 to 2.4 µg of magnesium per milliliter of solution in clay materials. In this range, the relative standard deviation of the method is 2 percent.

II. Principle of Method

In atomic absorption spectrometry, the analyte of the test portion is converted to an atomic vapor, and the absorption of light by the ground state atoms in the vapor phase is measured at the specific wavelength which is characteristic of the element. The light source is generally a hollow-cathode lamp adjusted to give an intense and sharp resonance line. Many parameters affect the production of atoms in flame gases. For many elements, the number of ground state resonance atoms will depend not only on the temperature of the flame, but on whether the fuel mixture results in a reducing or oxidizing flame. The concentration of free atoms often varies with the height of observation above the burner tip.

III. Interferences

The interferences in atomic absorption spectrometry are spectral, physical and chemical in nature. Usually spectral interferences are associated with the source of radiation—the hollow-cathode lamp. The filler gas in a hollow-cathode lamp, as well as impurities in the cathode material, will emit its characteristic radiation which may interfere with the analytical line. Spectral interferences from the source can be controlled by determining the constituents within the lamp and by selecting the proper optical condition to minimize or eliminate this interference.

Physical interferences may alter processes within the flame gases. These include aspiration, nebulization, solvent evaporation and vaporization. By selecting the

proper oxidant-fuel gas and burner system, these types of interferences can be minimized.

The greatest number of interferences in atomic absorption are of a chemical nature. Chemical interferences affect the analyte and may occur in the vapor, solid or liquid phase within the flame. Reactions occurring in the vapor phase may suppress or enhance the dissociation of the molecular species into atomic vapor. This is referred to as the condensed—phase interference. To control this type of interference, the oxidant-fuel and nebulizer-burner system must be carefully regulated. To overcome condensed phase types of interference, protective chelating agents can be used. Another approach for minimizing these interferences is by using high temperature flames such as the nitrous oxide-acetylene mixture; however, high temperature flames produce excessive ionization, which is undesirable. Chemical interferences can be overcome most satisfactorily by premixing the oxidant, air-nitrous oxide, in the proper ratio to provide the proper flame temperature.

IV. Reagents

(a) Magnesium, Standard Solution A (1 ml ≃ 10.0 mg Mg). Transfer 1.0000 ± 0.0005g of high purity magnesium metal to a 150-ml beaker. Add 50 ml of water. Slowly add 6 ml of HCl. After dissolution of the sample, transfer to a 100-ml volumetric flask, dilute to volume with water and mix.

(b) Magnesium, Standard Solution B (1 ml ≃ 40 µg Mg). Using a pipet, transfer 1 ml of Solution A (1 ml ≃ 10.0 mg Mg) to a 250-ml volumetric flask, dilute to volume with 0.1M HCl, and mix.

(c) Lanthanum, Standard Solution (1 ml ≃ 10.0 mg La). Transfer 11.73g of La_2O_3 to a 100-ml beaker. While stirring, add 20 ml of HCl and heat to dissolve. Cool, add

90 ml of $HClO_4$ and heat to fumes. Cool, transfer to a 1-liter volumetric flask, dilute to volume with water, and mix.

(d) Glycerol Solution (50 v/v percent, alkaline-earth free). Transfer 500 ml of analytical-reagent grade glycerol to a 1-liter volumetric flask and dilute to volume with water. Prepare an ion-exchange resin column by mixing an equal weight of Dowex 50-X8 (50 to 100 mesh) and Dowex 1-X10 (50 to 100 mesh) in a beaker. Wash with 6M HCl and then with water. Transfer the resin to a 1 x 15-cm glass column to provide a bed 10 cm in depth. Pass the glycerol solution through the column and collect for subsequent use.

V.   Preparation of Calibration Curve

1.   Using pipets, transfer 0, 1, 2, 3, 4 and 5 ml of Solution B (1 ml ≃ 40 μg Mg) to 100-ml volumetric flasks and dilute to about 50 ml with water.

2.   To each solution, add 10 ml of the standard solution of lanthanum and 20 ml of the purified glycerol solution.

3.   Dilute the flasks to volume with water, and mix. The solutions will contain 1000 μg of lanthanum/ml in 0.1N $HClO_4$ and 10 percent glycerol.

4.   Install the magnesium hollow-cathode lamp in the atomic absorption instrument.

5.   Set the current at two-thirds of the maximum operating current.

6.   Turn on the operating switches of the atomic absorption instrument and allow the hollow-cathode lamp to warm up for 15 min.

7.   Set the slit width at 50 μ and the voltage to the multiplier phototube (R-106) at 500 V.

8.   Install the premixed-laminar flow burner equipped with a 10-cm head within the flame housing.

9. Open the valves to the oxidant (air) and fuel (acetylene) cylinders and set the tank regulators at 40 and 15 psi, respectively.

10. Align the burner within the optical path of the light source.

11. Ignite the burner and adjust the pressure and/or flow rates to produce a reducing flame. Note. Observe the manufacturer's safety precautions in lighting the premixed burner.

12. Adjust the wavelength dial of the monochromator to Aspirate water between each standard and record the absorbance.

13. Adjust the gain of the operational amplifier to 100 percent transmission and the dark current to zero.

14. Aspirate the magnesium solution with the highest concentration (1 ml ≃ 2 µg Mg) from the series prepared in Step 1 and adjust the height and alignment to give the maximum absorbance.

15. Aspirate each calibration solution, in turn, including the reagent blank, and record the absorbance. Aspirate water between each standard and record the absorbance.

16. Plot the absorbance values, corrected for reagent blanks, etc. against micrograms of magnesium per milliliter, on rectangular coordinate paper. (The calibration curve should pass through the origin, but may deviate at higher concentrations of the analyte.)

VI. Procedure

1. Transfer to two 10-ml volumetric flasks, A and B, two equal test portions containing 4 to 12 µg of magnesium.

2. To test portion A, add 1 ml of the standard solution of lanthanum (1 ml ≃ 10 mg La), 2 ml of glycerol, dilute to volume with water, and mix.

3. To test portion B, add 4 µg of magnesium, 1 ml of the standard solution of lanthanum (1 ml $\simeq$ 10 mg La), 2 ml of glycerol, dilute to volume with water, and mix.

4. Aspirate test portions, A and B, and measure the absorbance of each.

5. From the calibration curve, determine the magnesium concentrations, µg/ml.

6. Recheck the calibration curve with standard solutions of magnesium.

7. Subtract the concentration, µg/ml, that was added to test portion B. If the concentrations of the two test portions agree, proceed to step 8. If the recoveries do not agree, correct by the standard addition method, and proceed to step 8.

8. Calculate the percent magnesium as follows:

$$\text{MgO, weight percent} = \frac{C \text{ X } Z \text{ X } 1.658}{W \text{ X } 10^4}$$

where:

C = magnesium concentration, µg/ml

Z = dilution factor

W = test portion of solid sample, grams.

CALCIUM BY ATOMIC ABSORPTION SPECTROMETRY

I   Scope

This atomic absorption method is applicable to the determination of 0.2 to 1.0 µg of calcium per milliliter of solution in clay materials. In this range, the relative standard deviation of the method is 2 percent.

II.   Principle of Method

See Section II of Magnesium Method.

III.   Interferences

See Section III of Magnesium Method.

IV.   Reagents

(a) Calcium, Standard Solution A (1 ml ≃ 10.0 mg Ca). Dry approximately 3 grams of $CaCO_3$ (NBS-915) at 110 °C for 2 hrs. Cool in a desiccator. Transfer 2.497 ± 0.001g of the dry $CaCO_3$ to a 100-ml volumetric flask. Slowly add 55 ml of ultra pure 1M HCl and warm to dissolve. Swirl the solution to expel CO_2, dilute to volume with 0.1M HCl, and mix.

(b) Calcium, Standard Solution B (1 ml ≃ 20 µg Ca). Using a pipet, transfer 1 ml of Solution A (1 ml ≃ 10.0 mg Ca) to a 500-ml volumetric flask, dilute to volume with 0.1M HCl, and mix.

(c) Aluminum, Standard Solution (1 ml ≃ 10.0 mg Al). Transfer 5.0 grams of aluminum metal (NBS 44e) to a 400-ml beaker. Add 50 ml of water and 40 ml of HCl. Warm to dissolve, cool, transfer to a 500-ml volumetric flask. Dilute to volume with water, and mix.

(d) Potassium, Standard Solution (1 ml ≃ 10.0 mg K). Transfer 9.5 grams of KCl to a 500-ml volumetric flask. Add 200 ml of water and 10 ml of 1M HCl. Dilute to volume with water, and mix.

V.   Preparation of Calibration Curve

1. Using pipets, transfer 0, 1, 2, 3, 4 and 5 ml of Solution B (1 ml ≃ 20 µg Ca) to 100-ml volumetric flasks, and dilute to about 50 ml with water.

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2. To each flask, add 5 ml of the standard solution of potassium and 5 ml of the standard solution of aluminum.

3. Dilute to volume with water, and mix. The solutions will contain 500 µg of potassium and aluminum/ml.

4. Install the calcium hollow-cathode lamp in the atomic absorption instrument.

5-7. Proceed as directed in steps 5 to 7 of Section V of the Magnesium Method. See page 63.

8. Install the premixed-laminar flow burner equipped with a 5-cm head (N_2O) in the flame housing.

9-10. Proceed as directed in steps 9 and 10 of Section V of the Magnesium Method.

11. Ignite the air-acetylene burner and adjust the flame to fuel rich conditions by gradually introducing C_2H_2. Then introduce N_2O and C_2H_2 until the N_2O ratio to air is 80-20. Note. Observe the manufacturer's safety precautions in the use of the nitrous oxide-acetylene flame.

12. Adjust the wavelength dial of the monochromator to the resonance line of calcium at 4227 Å to yield a maximum reading.

13. Proceed as directed in steps 13 to 16 of Section V of the Magnesium Method. See page 64.

VI. Procedure

1. Transfer to two 25-ml volumetric flasks, A and B, two equal test portions containing 5 to 15 µg of calcium.

2. Dilute test portion A to volume with water and mix.

3. To test portion B, add 8 µg of calcium, dilute to volume with water, and mix.

4. Aspirate test portions, A and B, and measure the absorbance of each.

5. From the calibration curve, determine the calcium concentration, µg/ml.

6. Recheck the calibration curve with standard solutions of calcium.

7. Subtract the concentration, µg/ml, that was added to test portion B. If the concentrations of the two test portions A and B agree, proceed to step 8. If the recoveries do not agree, correct by the standard addition method, and proceed to step 8.

8. Calculate the percent calcium as follows:

$$\text{CaO, weight percent} = \frac{C \times Z \times 1.399}{W \times 10^4}$$

where:

C = calcium concentration, µg/ml

Z = dilution factor

W = test portion of solid sample, grams.

STRONTIUM BY ATOMIC ABSORPTION SPECTROMETRY

I. Scope

This atomic absorption method is applicable to the determination of 1 to 5 μg of strontium per milliliter of solution in clay materials. In this range, the relative standard deviation of the method is 2 percent.

II. Principle of Method

See Section II of Magnesium Method.

III. Interferences

See Section III of Magnesium Method.

IV. Reagents

(a) Strontium, Standard Solution A (1 ml ≃ 10.0 mg Sr). Dry approximately 2 grams of reagent grade $SrCO_3$ at 110 °C for 2 hrs. Cool in a desiccator. Transfer 1.685 ± 0.001g of the dry $SrCO_3$ to a 100 ml volumetric flask. Slowly add 50 ml of ultra pure 1$\underline{M}$ HCl and warm to dissolve. Swirl the solution to expel CO_2, dilute to volume with 0.1$\underline{M}$ HCl, and mix.

(b) Strontium, Standard Solution B (1 ml ≃ 100 μg Sr). Using a pipet, transfer 1 ml of Solution A (1 ml ≃ 10.0 mg Sr) to a 100-ml volumetric flask, dilute to volume with 0.1$\underline{M}$ HCl, and mix.

(c) Aluminum, Standard Solution (1 ml ≃ 10.0 mg Al). Proceed as directed in Section IV of Calcium Method. See page 66.

(d) Potassium, Standard Solution (1 ml = 10.0 mg K). Proceed as directed in Section IV of Calcium Method. See page 66.

V. Preparation of Calibration Curve

1. Using pipets, transfer 0, 1, 2, 3, 4 and 5 ml of Solution B (1 ml ≃ 100 μg Sr) to 100-ml volumetric flasks, and dilute to about 50 ml with water.

2. To each flask, add 5 ml of the standard solution of potassium and 5 ml of the standard solution of aluminum.

3. Dilute to volume with water, and mix. The solutions will contain 500 μg of potassium and aluminum/ml.

4. Install the strontium hollow-cathode lamp in the atomic absorption instrument.

5-7. Proceed as directed in steps 5 to 7 of Section V of the Magnesium Method. See page 63.

8. Install the premixed-laminar flow burner equipped with a 5-cm head (N_2O) in the flame housing.

9-10. Proceed as directed in Steps 9 to 10 of Section V of the Magnesium Method. See page 64.

11. Ignite the air-acetylene burner and adjust the flame to fuel rich conditions by gradually introducing C_2H_2. Then introduce N_2O and C_2H_2 until the N_2O ratio to air is 80-20. Note. Observe the manufacturers safety precautions in the use of the nitrous oxide-acetylene flame.

12. Adjust the wavelength dial of the monochromator to the resonance line of strontium at 4607 Å to yield a maximum reading.

13. Proceed as directed in Steps 13 to 16 of Section V of the Magnesium Method. See page 64.

VI. Procedure

1. Transfer to two 25-ml volumetric flasks, A and B, two equal test portions containing 25 to 50 μg of strontium.

2. Dilute test portion A to volume with water and mix.

3. To test portion B, add 25 μg of strontium, dilute to volume with water, and mix.

4. Aspirate test portions, A and B, and measure the absorbance of each.

5. From the calibration curve, determine the strontium concentrations, μg/ml.

6. Recheck the calibration curve with standard solutions of strontium.

7. Subtract the concentration, μg/ml, that was added to test portion B. If the concentrations of the two test portions agree, proceed to step 8. If the recoveries do not agree, correct by the standard addition method, and proceed to step 8.

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8. Calculate the percent strontium as follows:

$$\text{SrO, weight percent} = \frac{C \times Z \times 1.183}{W \times 10^4}$$

where:

C = strontium concentration, $\mu g/ml$

Z = dilution factor

W = test portion of solid sample, grams.

BARIUM BY FLAME EMISSION SPECTROMETRY

I. **Scope**

This flame emission method is applicable to the determination of 0.5 to 2.5 µg of barium per milliliter of solution in clay materials. In this range, the relative standard deviation of the method is 2 percent.

II. **Principle of Method**

Barium is excited to emission in a nitrous oxide, air (80-20)-acetylene flame and is then determined by measuring the radiation intensity of the light emitted at a wavelength of 5536 Å.

III. **Interferences**

The resonance line of barium at 5536 Å suffers from serious spectral interference of the CaO-CaOH band system when a low temperature flame is used. Using a high temperature flame such as nitrous oxide-acetylene, the interference is minimized. The magnitude of the interference will depend upon the resolution of the monochromator.

IV. **Reagents**

(a) Barium, Standard Solution A (1 ml ≈ 10.0 mg Ba). Dry 2 grams of reagent grade $BaCO_3$ at 110 °C for 2 hrs. Cool in a desiccator. Transfer 1.437g $\pm$ 0.001g of the dry $BaCO_3$ to 100-ml volumetric flask. Add 40 ml of 1$\underline{M}$ HCl and warm to dissolve. Swirl the solution to expel CO_2, dilute to volume with 0.1$\underline{M}$ HCl, and mix.

(b) Barium, Standard Solution B (1 ml ≈ 50 µg Ba). Using a pipet, transfer 1 ml of Solution A (1 ml ≈ 10.0 mg Ba) to a 200-ml volumetric flask, dilute to volume with 0.1$\underline{M}$ HCl, and mix.

(c) Aluminum, Standard Solution (1 ml ≈ 10.0 mg Al). Prepare as directed in Section IV of the Calcium Method. See page 66.

(d) Potassium, Standard Solution (1 ml ≈ 10.0 mg K). Prepare as directed in Section IV of the Calcium Method. See page 66.

V.   Preparation of Calibration Curve

1.   Using pipets, transfer 0, 1, 2, 3, 4 and 5 ml of Barium Solution B (1 ml ≈ 50 µg Ba) to 100 ml volumetric flasks, and dilute to about 50 ml with water.

2.   To each flask, add 5 ml of the standard solution of potassium and 5 ml of the standard solution of aluminum.

3.   Dilute to volume with water, and mix.

4.   Turn on the operating switches of the flame emission spectrometer.

5.   Set the voltage to the multiplier phototube at 1400 V.

6.   Install the premixed laminar flow burner equipped with a 5-cm head (N_2O) in the flame housing.

7.   Ignite the air-acetylene burner and adjust the flame to fuel rich conditions by gradually introducing C_2H_2. Then introduce N_2O and C_2H_2 until the N_2O ratio to air is 80-20. Note. Observe the manufacturer's safety precautions in the use of the nitrous oxide-acetylene flame.

8.   Set the wavelength of the monochromator to 5536 $\overset{\circ}{A}$ and the slit width at 50 µ .

9.   Aspirate the barium solution with the highest concentration (1 ml ≈ 2.5 µg Ba) from the series prepared in step 1.

10.   Adjust the gain of the operational amplifier to give 85 percent of full scale, as indicated on the recorder.

11.   While aspirating set the wavelength of the monochromator at 5530 $\overset{\circ}{A}$ and scan the barium line at 5536 $\overset{\circ}{A}$ at a rate of 10 $\overset{\circ}{A}$/min.

12.   Repeat step 10 with each calibration solution, in turn, and record its radiation intensity. Aspirate water between each standard solution and record the radiation intensity.

13.   Plot the radiation intensity values, corrected for background, against micrograms of barium per milliliter, on rectangular coordinate paper.

VI. Procedure

    1. Transfer to two 25-ml volumetric flasks, A and B, two equal test portions containing 15 to 30 µg of barium.

    2. Dilute test portion A to about 15 ml with water, add 1 ml of standard solution of potassium, dilute to volume with water and mix.

    3. To test portion B, add 15 µg of barium, 1 ml of standard solution of potassium, dilute to volume with water and mix.

    4. Aspirate test portions, A and B, and measure the radiation intensity of each.

    5. From the calibration curve, determine the barium concentrations, µg/ml.

    6. Recheck the calibration curve with standard solutions of barium.

    7. Subtract the concentration, µg/ml, that was added to test portion B. If the concentrations of the two test portions agree, proceed to step 8. If the recoveries do not agree correct by the standard addition method, and proceed to step 8.

    8. Calculate the percent barium as follows:

$$\text{BaO, weight percent} = \frac{C \times Z \times 1.117}{W \times 10^4}$$

where:

    C = barium concentration, $\mu g/ml$

    Z = dilution factor

    W = test portion of solid sample, grams.

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APPENDIX 1

Certificate of Analysis

STANDARD REFERENCE MATERIAL 97a

Flint Clay

(Results based on sample dried for two hours at 140 °C)

Analyst	SiO₂	Al₂O₃	Fe₂O₃	TiO₂	P₂O₅	K₂O	Na₂O	Li₂O	ZrO₂	BaO	MgO	CaO	SrO	Cr₂O₃	Loss on Ignition
1[1]	43.74	38.65	{0.45[a] / .46[b]}	{1.88[c] / 1.89[d]}	0.34	0.53[e]	0.033[e]	0.12[e]	0.063[f]	0.078[e]	0.16[g]	0.11[g]	0.17[e]	0.028[h]	13.32
2[2]	43.68	38.95	.45	1.95	.35	.51[e]	.041[e]	.10[g]	-------	.07	.14[g]	.11[g]	.18[e]	.03	13.31
3	43.60	38.79	.43[a]	1.87[d]	.38[i]	.46[e]	------	------	------	------	------	------	------	------	------
Average	43.67	38.79	0.45	1.90	0.36	0.50	0.037	0.11	-------	0.07₅	0.15	0.11	0.18	0.03	13.32

References: [1] G.E.F. Lundell and J.I. Hoffman, NBS J. Res. 1, 91 (1928) RP5.
[2] L. C. Peck, Geological Survey Bulletin 1170, (1964).

[a] o-phenanthroline photometric method.
[b] Iron reduced with SnCl₂ and titrated with standard potassium dichromate solution.
[c] Cupferron gravimetric method.
[d] H₂O₂ photometric method.

[e] Flame emission spectrometric method.
[f] Pyrocatechol violet photometric method.
[g] Atomic absorption method.
[h] Diphenylcarbazide photometric method.
[i] Molybdenum-blue photometric method.

List of Analysts

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2. L. C. Peck, United States Geological Survey, Denver, Colorado.

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The material for the preparation of this standard was provided by the A. P. Green Fire Brick Company, Mexico, Missouri.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanships of O. Menis and J. I. Shultz.

The technical and support aspects involved in the preparation, certification and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

Washington, D. C. 20234
October 8, 1969

J. Paul Cali, Acting Chief
Office of Standard Reference Materials

APPENDIX 2

Certificate of Analysis

STANDARD REFERENCE MATERIAL 98 a

Plastic Clay

(Results based on sample dried for two hours at 140 °C)

Analyst	SiO₂	Al₂O₃	Fe₂O₃	TiO₂	P₂O₅	K₂O	Na₂O	Li₂O	ZrO₂	BaO	MgO	CaO	SrO	Cr₂O₃	Loss on Ignition
1 [1]	48.98	33.13	{1.34ᵃ} {1.37ᵇ}	{1.56ᶜ} {1.63ᵈ}	0.11	1.07ᵉ	0.080ᵉ	0.075ᵉ	0.042ᶠ	0.031ᵉ	0.42ᵉ	0.31ᵉ	0.041ᵉ	0.030ʰ	12.40
2 [2]	48.91	33.31	1.35	1.64	.10	1.08ᵉ	.083ᵉ	.064ᵍ	_____	.03	.43ᵉ	.31ᵉ	.037ᵍ	.04	12.49
3	_____	33.12	1.28ᵃ	1.61ᵈ	.11ⁱ	0.98ᵉ	_____	_____	_____	_____	_____	_____	_____	_____	_____
Average	48.94	33.19	1.34	1.61	0.11	1.04	0.082	0.070	_____	0.03	0.42	0.31	0.039	0.03	12.44

References: [1] G.E.F. Lundell and J.I. Hoffman, NBS J. Res. 1, 91 (1928) RP5.
[2] L.C. Peck, Geological Survey Bulletin 1170, (1964).

ᵃo-phenanthroline photometric method.
ᵇIron reduced with SnCl₂ and titrated with standard potassium dichromate solution.
ᶜCupferron gravimetric method.
ᵈH₂O₂ photometric method.

ᵉFlame emission spectrometric method.
ᶠPyrocatechol violet photometric method.
ᵍAtomic absorption method.
ʰDiphenylcarbazide photometric method.
ⁱMolybdenum-blue photometric method.

List of Analysts

1. R. K. Bell, B. B. Bendigo, T. C. Rains, T. A. Rush, E. R. Deardorff, J. R. Baldwin, R. A. Paulson, W. P. Schmidt, and S. D. Rasberry, Analytical Chemistry Division, Institute for Materials Research, National Bureau of Standards.

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This publication brings together a compilation of methods used at NBS for the analysis of two complex standard reference clay materials. The methods were selected to give the best obtainable results for those elements normally found in clays. In some instances, more than one procedure was employed for an element as a cross-check on the precision and accuracy of the results. The procedures are presented in two parts. Part I is concerned with the determination of the major constituents by the classical analytical procedures. Part II covers the minor elements which are determined instrumentally by flame emission and atomic absorption spectrometry. These clay materials serve as analytical composition standards to provide quality control of the basic raw materials which are used in the ceramics and refractories industries.

17. KEY WORDS (Alphabetical order, separated by semicolons) Atomic absorption; ceramics; classical procedures; clay materials; flame emission; refractories; Standard Reference Materials.

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