METHODS OF SOIL AND PLANT ANALYSIS

With Special Reference to Strontium 90 Contamination

Agriculture Handbook No. 288

Agricultural Research Service
UNITED STATES DEPARTMENT OF AGRICULTURE

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Washington, D.C. Issued August 1965

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This handbook contains procedures for determining soil properties necessary to the uptake of strontium 90 from soil by plants. By these methods can be determined the amount and kind of exchangeable cation, pH, and amount of organic matter in soil, as well as the amount of major cation and strontium content of plants. The application of the analytical results obtained is not discussed, because it depends primarily on the purpose for which the samples were taken.

The procedures were taken directly from the literature or were developed in part or entirely by the U.S. Soils Laboratory. Caution should be used in universally applying these procedures, since some of them were developed for specific materials. This is especially true for strontium determination, both natural and radioactive, in that interference from other elements might have different effects on materials other than plants and soils.

PREPARATION OF SAMPLES

Soil samples are prepared for determination of exchangeable alkali and alkaline earth cations by extraction with ammonium acetate. Separate soil samples are used for determination of pH, organic matter content, and exchangeable hydrogen. A much larger sample is used for determination of available and fixed strontium 90.

Spread the field sample (at least 10 pounds) of soil on heavy paper and allow to dry until it can be crushed and sieved easily. Sieve the soil through a quarter-inch mesh screen. Mix before subsampling by rolling on a large sheet of paper. Discard large roots, rocks, and other extraneous material after weighing.

Samples of plant materials should be dried for preservation and better subsampling. Air-drying may be satisfactory, but drying in a forced-draft low-temperature oven (below 70° C.) is preferred. Air-dried samples require a moisture determination and, in some cases, certain parts of the plant will not dry in a reasonable time. Cutting thick plant parts such as petioles, stems, or roots into small segments or slices will greatly increase their drying rate. Unless the

[1] The preparation of this handbook was supported in part by the U.S. Atomic Energy Commission.

entire sample is to be analyzed, the plant material must be finely ground to facilitate proper subsampling. Also, the organic fraction of the plant material is much easier to destroy if the sample is finely divided. The grinding is usually done in a Wiley mill [2] or similar apparatus, using a 30- or 40-mesh screen.

Plant materials are prepared for analysis by dry combustion. This is recommended because large samples are usually required for determination of strontium 90 and they are much easier and safer to handle by dry combustion. The determination of alkali and alkaline earth cations may be made on aliquot parts of the sample taken after the ash has been dissolved.

Ammonium Acetate Extraction of Soil

Equipment

(1) Carboy—18 liters.
(2) Erlenmeyer flask—250 ml.
(3) Mechanical shaker.
(4) Suction flask—1 liter.
(5) Büchner funnel—No. 1 (5.6-cm. inside diameter).
(6) Filter paper—Whatman No. 42 or equivalent (5.5-cm. diameter).
(7) Spatula.
(8) Beaker—400 ml.
(9) Fluted watchglass.
(10) Hotplate.
(11) Volumetric flask—100 ml.

Reagents

(1) Neutral ammonium acetate (NH_4OAc), 1 *N*: Mark the carboy at the 18–liter level. Fill it three-fourths full with distilled water. Add 1,037 ml. of concentrated acetic acid (HOAc) and 1,215 ml. of concentrated ammonium hydroxide (NH_4OH). After mixing and cooling this solution, measure the pH of a small aliquot. If acid, return the aliquot to the carboy and add 5 to 10 ml. of concentrated ammonium hydroxide, mix thoroughly, and take the pH reading again. Decrease the amount of ammonium hydroxide used as the pH approaches 7. If the solution is basic, add small increments of concentrated acetic acid in place of ammonium hydroxide. If the solution is only slightly basic, bubbling air through the solution for several hours usually lowers the pH to 7. Dilute to a volume of 18 liters.

(2) Nitric acid (HNO_3)—concentrated, reagent grade.
(3) Perchloric acid ($HClO_4$)—concentrated, reagent grade.
(4) Nitric acid, 0.1 *N*: Dilute 114.5 ml. of concentrated nitric acid and make up to 18 liters in a carboy with distilled water.

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[2] Trade names are used in this publication solely for the purpose of providing specific information. Mention of a trade name does not constitute a guarantee or warranty of the product by the U.S. Department of Agriculture or an endorsement by the Department over other products not mentioned.

Procedure

Put 25 g. of the sieved sample into a 250-ml. Erlenmeyer flask; add 100 ml. of 1 *N* neutral ammonium acetate, stopper, and let stand overnight. Larger amounts of soil should be extracted if the texture is very sandy or if the soil is very acid. Increase the amount of soil proportionately as the amount of extracting solution is increased. For best results, mix the sample by frequent shaking, either by hand or in a mechanical shaker.

Set in place a 1-liter suction flask and a Büchner funnel containing a circle of Whatman No. 42 filter paper, 5.5 cm. in diameter. Add a small amount of water to the funnel and apply suction until the paper is set. Do not allow the paper to become dry. Rapidly swirl the soil and ammonium acetate mixture. Pour enough of this mixture on the set filter paper to just cover the paper, allow to stand for a few seconds, and then turn on the suction. When this solution has been pulled through, add the rest of the suspension rapidly. If this procedure is done carefully, the filtrate will be clear. If the filtrate is cloudy, turn off the suction and pour the filtrate back in the funnel. This may have to be done several times with some soils. Mix the remaining suspension in the flask and add to the Büchner funnel when possible. Soil allowed to become dry may develop cracks and consequently will not leach properly. If cracks develop, use a spatula to close them before adding more liquid.

Rinse the Erlenmeyer flask with small amounts of ammonium acetate and add the rinse to the Büchner funnel when no more liquid is standing on the soil, but before it becomes dry. Continue rinsing until 250 ml. of leachate is collected in the suction flask. Allow the soil to drain well before stopping suction.

Pour the leachate into a 400-ml. beaker and rinse the suction flask several times with distilled water, adding the rinses to the beaker. Cover the beaker with a fluted watchglass. Evaporate the solution to dryness on a hotplate. When the material is dry, add 20 ml. of concentrated nitric acid and 5 ml. of concentrated perchloric acid and evaporate to dryness again. One acid treatment should destroy the organic matter. If not, again add 10 ml. of concentrated nitric acid and 2 ml. of concentrated perchloric acid and evaporate to dryness. When the beaker is cool, add about 50 ml. of 0.1 *N* nitric acid, which should dissolve most of the solids. Filter through Whatman No. 42 filter paper into a 100-ml. volumetric flask. Wash the beaker and residue with small amounts of 0.1 *N* nitric acid until almost 100 ml. of solution is collected in the volumetric flask. Make to volume with distilled water and mix thoroughly.

Ashing of Plant Material

Equipment

(1) Porcelain evaporating dish—No. 9 (265-mm. diameter).
(2) Electric muffle furnace, with automatic temperature control.
(3) Watchglass (12-inch diameter).
(4) Hotplate.
(5) Funnel—long stem (100-mm. outside diameter).

(6) Filter paper—Whatman No. 42 or equivalent (18.5-cm. diameter).
(7) Volumetric flask—500 ml.
(8) Erlenmeyer flask—250 ml.

Reagents

(1) Hydrochloric acid (HCl)—concentrated, reagent grade.
(2) Hydrochloric acid, 1 *N*: Dilute 85 ml. of concentrated hydrochloric acid to a volume of 1 liter with distilled water.

Procedure

Ash the plant material in an electric muffle furnace at 550° C. for 16 hours. Two hundred grams of plant material can conveniently be ashed in a No. 9 porcelain evaporating dish. The ash should be white if oxidation of the organic material is complete. Gray or dark-colored ash indicates incomplete oxidation. Remuffling after cooling and aeration will oxidize the sample more completely.

Place a 12-inch watchglass on the porcelain dish, leaving a small opening through which enough distilled water is added to moisten the ash. Then add concentrated hydrochloric acid to cover the ash. This procedure minimizes loss of ash caused by splattering. After the reaction has subsided, rinse the material on the watchglass into the porcelain dish. Place the uncovered dish on the hotplate and evaporate carefully to dryness. Cool and dissolve the sample with several hundred milliliters of 1 *N* hydrochloric acid. Filter through Whatman No. 42 filter paper, using a long-stem funnel. Wash the dish and undissolved material collected on the filter paper with additional 1 *N* hydrochloric acid until a volume of 500 ml. is collected in the volumetric flask. Discard the undissolved residue.

Put a 100-ml. sample from 500 ml. of the ash extract in a 250-ml. Erlenmeyer flask. Keep for determination of alkali and alkaline earth cations. The remaining 400 ml. is used for the determination of strontium 90.

DETERMINATIONS ON AMMONIUM ACETATE EXTRACTS OF SOIL AND SOLUTIONS OF PLANT ASH

Calcium and Magnesium

Equipment

(1) Pipets—1, 5, 15, and 20 ml.
(2) Beakers—250 ml.
(3) Microburet.
(4) Fluorescent lamp.
(5) Magnetic stirrer and stirring bar (optional).
(6) pH meter.
(7) Hydrion paper.
(8) Funnel—long stem (7.0-cm. outside diameter).
(9) Hotplate.
(10) Filter paper—Whatman No. 42 or equivalent (5.5-cm. diameter).

Reagents

(1) Standard calcium solution: Dissolve 0.5004 g. of special "low magnesium" reagent grade calcium carbonate ($CaCO_3$), dried at 150° C., in 5 ml. of approximately 6 *N* hydrochloric acid (HCl) and dilute to a volume of 1 liter. This solution is 0.005 molar.

(2) Buffer solution: Dissolve 67.5 g. of ammonium chloride (NH_4Cl) in 200 ml. of distilled water, add 570 ml. of concentrated ammonium hydroxide (NH_4OH), and dilute the solution to a volume of 1 liter with distilled water.

(3) Masking reagents (each of the following solutions must be stored in separate containers):

(a) Cyanide solution: Dissolve 1 g. of potassium cyanide (KCN) in 100 ml. of distilled water.

(b) Hydroxylamine-hydrochloride solution: Dissolve 5 g. of hydroxylamine-hydrochloride ($NH_2OH \cdot HCl$) in 100 ml. of distilled water.

(c) Potassium ferrocyanide solution: Dissolve 4 g. of reagent grade potassium ferrocyanide ($K_4Fe(CN)_6 \cdot 3H_2O$) in 100 ml. of distilled water.

(d) Triethanolamine—reagent grade.

(4) Eriochrome Black T. indicator: Dissolve 0.2 g. of Eriochrome Black T. (EBT) in 50 ml. of methanol. Prepare a fresh solution every 3 weeks.

(5) Standard EDTA solution: Dissolve 1.8613 g. of disodium ethylenediaminetetraacetate (EDTA) (molecular weight=372.254) in distilled water and dilute the solution to a volume of 1 liter. This solution is 0.005 molar. Its titer will change if stored in glass containers but not in polyethylene.

(6) Standard magnesium solution: Dissolve 0.1216 g. of reagent grade magnesium turnings in dilute hydrochloric acid and dilute to a volume of 1 liter. This solution is 0.005 molar.

(7) Calcon indicator: Dissolve 20 mg. of Calcon in 50 ml. of methanol. Prepare a fresh solution weekly.

(8) Sodium hydroxide, 10-percent solution: Dissolve 10 g. of reagent grade sodium hydroxide (NaOH) in 100 ml. of distilled water.

(9) Sodium tungstate solution: Dissolve 20 g. of sodium tungstate ($Na_2WO_4 \cdot 2H_2O$) in 100 ml. of distilled water.

Procedure (*1, 2, 3, 4, 9*) [3]

Standardization of EDTA.—Pipet 5-ml. aliquots of the standard calcium solution into each of three 250-ml. beakers and bring the volume to approximately 150 ml. with distilled water. Pipet 15 ml. of buffer solution, 10 drops of each masking reagent, and 10 drops of EBT indicator. Titrate the solution with EDTA, with stirring, to a permanent blue, using a microburet under a fluorescent lamp. Although stirring by hand is satisfactory, the use of a Teflon-coated magnetic stirring bar activated by a magnetic stirring apparatus is much more convenient. Repeat titration with three 5-ml. aliquots of standard magnesium solution. This standard serves to check the validity of the calcium titration.

[3] Italic numbers in parentheses refer to Literature Cited, p. 23.

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The EDTA should also be standardized, using Calcon as the indicator. Pipet three 5-ml. aliquots of standard calcium solution into three 250-ml. beakers and bring the volume to approximately 150 ml. with distilled water. Add 10 drops of each masking reagent, then pipet 1 ml. of 10-percent sodium hydroxide or an amount sufficient to raise the pH to 12 or slightly higher. Check with a pH meter or Hydrion paper. Add 5 drops of Calcon indicator and titrate from a red to a permanent blue with EDTA under the same conditions as above. All microburet readings should agree within 0.05 ml.

Titrate three blanks with each standardization. The EDTA should be standardized every time a new set of samples is to be titrated. This titration not only rechecks the standardization of the EDTA but also indicates the presence of contamination in the microburet, pipets, and beakers.

Calcium Plus Magnesium.—Place an aliquot containing 1 to 2 mg. of calcium plus magnesium in a 250-ml. beaker and dilute to about 150 ml. with distilled water. Pipet 15 ml. of buffer solution and 10 drops of each masking reagent. Allow a few minutes for the reactions to take place, especially for the formation of manganese ferrocyanide. Warming will speed this reaction. Add 10 drops of the EBT indicator and titrate in the same manner and to the same color as when the EDTA was standardized.

If the end point is difficult to obtain, probably too much phosphate is present. (See comments.) To overcome this difficulty, use the following procedure: To a new aliquot, add 10 drops of each masking reagent as before. Add a known excess amount of the standardized EDTA. Experience will indicate the amount of EDTA necessary. Bring the solution to the necessary pH value by adding 15 ml. of the buffer solution. The pH of this solution should be 10. If there is any doubt because of high salt or acid content in the original aliquot, check with the pH meter and add more buffer to bring to pH 10. Heat the solution on a hotplate to near boiling for several minutes to speed up the reaction, cool, add 10 drops of EBT indicator, and titrate from a blue to a permanent red with the standard calcium solution.

Calcium.—Place an aliquot containing 1 to 2 mg. of calcium in a 250-ml. beaker and dilute to a volume of about 150 ml. with distilled water. Add 10 drops of each masking reagent and enough 10-percent sodium hydroxide (usually about 1 ml.) to raise the pH to 12 or slightly higher. Check with a pH meter or Hydrion paper. Add 5 drops of Calcon indicator and titrate the solution from red to blue with standardized EDTA.

If the end point is difficult to obtain because of the presence of phosphate, to a new sample add the masking reagents and a known but an excess amount of EDTA. Bring the pH up slowly to 12 with 10-percent sodium hydroxide. Then heat the solution to near boiling for several minutes, cool it, add 5 drops of Calcon indicator, and titrate the solution from blue to red with a standard calcium solution.

Magnesium.—Place an aliquot containing 2 to 4 mg. of magnesium in a 250-ml. beaker and add enough distilled water to make a total volume of about 100 ml. Pipet 20 ml. each of the buffer solution and sodium tungstate solution. Check with a pH meter and add more buffer solution to bring to pH 10. Heat the beaker and contents for 1 hour without boiling, cool, and filter the contents through Whatman No. 42 filter paper. Wash the paper and precipitate with a solution

containing 50 ml. of buffer solution per liter. Add 10 drops of each masking reagent. Allow a few minutes for the reactions to take place. Add 10 drops of the EBT indicator and titrate from a red to a permanent blue. Heating slightly will speed the magnesium end point.

Calculation of Results.—If the EDTA solution has been carefully prepared from a pure material, the following relationships are true: Each milliliter of EDTA is equivalent to 0.005 mM of cation whether the cation is calcium, magnesium, or the sum of the two. Also, each milliliter of EDTA is equivalent to 0.2004 mg. of calcium or calcium plus magnesium expressed as calcium, or 0.1216 mg. of magnesium or calcium plus magnesium expressed as magnesium.

Since the commercial form of EDTA may contain varying amounts of adsorbed water and other impurities, the following equations are used to calculate the millimoles of calcium plus magnesium, calcium, or magnesium in the bulk sample, depending on the conditions under which the titration was made.

Standardization of EDTA:

$$\frac{\text{(Millimoles of standard cation used in titration)}}{\text{(Milliliters of EDTA}_{\text{standard}}\text{—milliliters of EDTA}_{\text{blank}}\text{)}} = \text{concentration of EDTA in terms of millimoles per milliliters}$$

Evaluation of sample:

Concentration of standardized EDTA × (milliliters of $\text{EDTA}_{\text{sample}}$—milliliters of $\text{EDTA}_{\text{blank}}$) × aliquoting factor = millimoles of cation in total sample

If an excess of EDTA was added to overcome phosphate interferences, these equations are used to obtain the total millimoles of cation in the sample. From this value subtract the number of millimoles of standard calcium used in the back titration, giving the millimoles of cation originally in the aliquot taken.

The usual procedure is to obtain the millimoles of calcium plus magnesium and then determine the millimoles of either calcium or magnesium. The millimoles of the other cation are obtained by subtraction.

Comments

The nature of the material may make some modifications necessary. The amounts of reagents used are sufficient for most conditions that may be encountered. However, in the presence of large amounts of iron or aluminum, more masking reagents may be required. It may be even necessary to remove a large excess of iron or aluminum by the classical hydroxide precipitation. When abnormally large amounts of phosphate are present, a separation or removal of phosphate is recommended before the titration. Increasing or decreasing the amount of indicator may help some workers to see the end point better.

As little as 10 p.p.m. of phosphate will interfere with the calcium titration. This concentration is rarely found in soil extracts, but it will be commonly found in plant tissue digests, particularly from seeds.

The stability constant of calcium phosphate is less than that of calcium-versenate; therefore, EDTA will dissolve calcium phosphate, but the process is slow. In the procedure generally used, calcium phosphate is formed before sufficient EDTA has been added. In the titration then a permanent blue, which indicates the end point, cannot be maintained while calcium phosphate is dissolving. This makes the titration impractical.

In some rare instances the magnesium concentration may be as large or larger than the calcium concentration, causing a poorly defined color change at the end point when titrating calcium alone. In this case, the calcium indicator is adsorbed on the magnesium hydroxide particles, making the color change many shaded and difficult to see. A protective colloid such as Carbocel may be added to prevent the adsorption of the dye (*10*). It has also been found that if most of the EDTA is added before the pH is raised, the color change at the end point is sharp and easily seen (*7*).

The amounts of extractable or total barium or strontium in some soils may be large enough to interfere. Although calcium may be separated from barium and strontium, the procedures are difficult. Both barium and strontium form EDTA complexes of low stability; therefore, unless their concentrations approach that of calcium, the degree of interference will be small.

Strontium by Flame Photometry

Equipment

(1) Equipment necessary for determining calcium.
(2) Pipets—5 and 10 ml., graduated, blowout type.
(3) Centrifuge tubes—40 ml., heavy duty.
(4) Water bath—2-liter beaker, with metal cover punched out to support centrifuge tubes.
(5) Centrifuge.
(6) Electric muffle furnace, with automatic temperature control.
(7) Fritted glass filter assembly: From a 15-ml., 20-mm. diameter, coarse porosity filter funnel (Corning, type 36060), remove the part above the glass frit with a glass saw and grind level the remaining frit. Cut a 5-cm. chimney from a length of glass tubing (18-mm. inner diameter) and grind one end level. Mount the filter funnel in a suction apparatus, place a filter pad on the fritted glass, and center the ground end of the chimney carefully over the fritted glass. During filtration, the assembly is held tightly together by means of rubber-bands and wire hooks.
(8) Suction apparatus—Nylab filter bell.
(9) Filter paper—glass-fiber or conventional paper (2.1-cm. diameter).
(10) Flame photometer—D.U. Beckman model, with photomultiplier attachment and hydrogen-oxygen burner assembly.
(11) Beakers—5 ml.

Reagents

(1) Strontium standard solutions: A series containing 0, 0.5, 1.0, 2.0, 2.5, 5, 7.5, and 10 p.p.m. of strontium and 500 p.p.m. of calcium is made up in 0. 1 *N* hydrochloric acid. A stock solution of strontium

chloride should be standardized by gravimetric determination of strontium sulfate. Standard calcium solution, as prepared for the determination of calcium (p. 4), may be used to make this series of strontium standards.

(2) Reagents necessary for determining calcium (p. 4).

(3) Hydrochloric acid, approximately 6 *N*: Dilute 500 ml. of concentrated hydrochloric acid (HCl) to a volume of 1 liter with distilled water.

(4) Oxalic acid, 5 percent: Dissolve 100 g. of oxalic acid ($H_2C_2O_4$) in 2 liters of distilled water.

(5) Indicator solution: Phenol red, 0.1 percent in 1:1 ethyl alcohol: Dissolve 0.1 g. of phenol red in 100 ml. of a solution containing 52 ml. of ethyl alcohol and 48 ml. of water. Methylene blue, 0.2 percent: Dissolve 20 mg. of methylene blue in 100 ml. of water. Mix these two solutions at a rate of one part of phenol red and two parts of methylene blue.

(6) Ammonium hydroxide: Dilute 250 ml. of concentrated ammonium hydroxide (NH_4OH) to a volume of 1 liter with distilled water.

(7) Washing solution: To make 1 liter, mix the following ingredients in the proportions given: 20 ml. of concentrated ammonium hydroxide, 326 ml. of distilled water, 326 ml. of ether, and 326 ml. of ethyl alcohol.

(8) Hydrochloric acid, 0.1 *N*: Dilute 17.2 ml. of concentrated hydrochloric acid to a volume of 2 liters with distilled water.

Procedure

The strontium determination is made on a solution containing 500 p.p.m. of calcium, which for convenience should have a volume of about 15 ml. From the following calculations the number of milliliters of soil or plant extract (see Preparation of Samples) needed is obtained.

(1) If milliequivalents of calcium per 100 g. of soil is known,

$$\frac{(\text{milliequivalents of calcium per 100 g. of soil})}{4} \times 20 = \text{milligrams per 100 ml.}$$

$$(\text{milligrams per 100 ml.}) \times 10 = \text{parts per million}$$

$$\frac{500 \times 15}{(\text{parts per million})} = \text{number of milliliters needed.}$$

Therefore,

$$\frac{150}{(\text{milliequivalents of calcium per 100 g. of soil})} = \text{aliquot.}$$

(2) If parts per million of calcium in the extract is known,

$$\frac{7{,}500}{(\text{parts per million of calcium})} = \text{aliquot.}$$

For convenience, take the aliquot to the nearest 0.5 ml. and adjust the final volume to contain 500 p.p.m.

Pipet the calculated aliquot into a 40-ml. centrifuge tube and dilute to about 20 ml. with distilled water. Add 1 ml. of 6 *N* hydrochloric acid and 2 ml. of 5-percent oxalic acid and place in a gently boiling water bath. Remove the tube from the bath after its contents have reached about 90° C. (equilibrium with boiling water bath) and add 5 drops of the mixed indicator solution. Add ammonium hydroxide dropwise, mixing continually with a swirling motion until the solution just changes from a green to a blue. Calcium oxalate should start precipitating shortly after the hydroxide is added. Replace the tube in the boiling water bath for 30 minutes. The addition of small amounts of ammonium hydroxide may be necessary from time to time to keep the suspension slightly basic (just blue). Cool the tube and suspension and centrifuge for 20 minutes at about 1,500 r.p.m.

Decant the supernate carefully and lay the tube on a slant for 10 minutes to facilitate drainage. Wipe the lip of the tube with a tissue to remove the last drops and suspend the oxalate precipitate by stirring with a jet of 5 ml. of washing solution. Centrifuge, decant, and drain once again.

Allow the precipitate to air-dry overnight. Heat the samples at least 1 hour at 525° C. in a muffle furnace. At this temperature calcium and strontium oxalate are converted to carbonates, also any iron or aluminum present is converted to the dehydrated oxides. When the samples are cool, dissolve the precipitate in 0.1 *N* hydrochloric acid. The number of milliliters of hydrochloric acid necessary is calculated to the nearest 0.01 ml. as follows:

$$\frac{(\text{Parts per million of calcium in original sample})}{500} \times \text{aliquot} = \text{milliliters of 0.1 } N \text{ hydrochloric acid required}$$

If iron, manganese, and aluminum were present in the original sample in any appreciable amounts, they will appear as precipitates in the sample and must be removed. The precipitates are easily removed by filtering. The removal is essentially quantitative if done shortly after the carbonate sample is dissolved. A fritted glass filter assembly with suction apparatus is convenient, in that the assembly may be rapidly washed with acid and dried with ether or alcohol between samples. The actual filtering surface may be either glass-fiber or conventional filter paper. Glass-fiber paper has the advantage of retaining little of the liquid fraction.

If the filtered sample is cloudy or colored, the sample should be refiltered or dried and muffled. When a clear solution is obtained, determine the calcium as previously described. If the initial titration or estimation of calcium, pipeting, and precipitation procedure were done properly, the calcium concentration should be 500 p.p.m. If the present titration is not within 20 p.p.m. of 500 p.p.m., the sample must be concentrated or diluted.

A D.U. Beckman photometer is used to estimate strontium in a hydrogen-oxygen flame. Allow at least a 30-minute warming-up period with the selector switch at check. Set the oxygen pressure at 10 p.s.i. and the hydrogen pressure at 3 p.s.i., with the control associated with the instrument, and light the flame. For stability of the pressures, it

is best to have at least 20-p.s.i. pressure showing on the low-pressure gages of the oxygen and hydrogen tanks. Use full photomultiplication and set the switch accordingly. The blue tube is set into position according to the instructions furnished by the manufacturer. Always keep the galvanometer at zero with the dark current control.

The following settings are made initially: Wavelength dial to 460.7 mμ, slit width at 0.03 mm., transmittance reading at 100, and sensitivity control at midpoint. Aspirate several 5-ml. beakers full of water. Place a 5-ml. beaker of the most concentrated standard solution in position to be aspirated. Open the shutter and move the wavelength dial slightly. A deflection of the galvanometer needle to the left indicates that the original wavelength setting was wrong. Adjust until a very slight turn of the dial in either direction results in the galvanometer needle deflecting to the right. Close the shutter after each reading and check the dark current setting.

Produce a standard curve as follows: Set the transmittance dial at 100 and aspirate the most concentrated standard. Zero the galvanometer needle with the dark current control, open the shutter, and zero the needle with the sensitivity control. Close the shutter, remove the sample, and rinse the burner with distilled water for a few seconds. Put the next most concentrated standard solution in position. Make the reading by moving the transmittance dial until the galvanometer needle is at zero. Reset the instrument at 100-percent transmission with the most concentrated standard solution before each new reading is made. Obtain transmittance readings for standards by this process. Plot the transmittance reading against the concentration of the standard and calculate the equation of the line.

Pour the unknown into a 5-ml. beaker and aspirate through the burner assembly for a few seconds. Discard the remainder, refill the beaker, and replace under the flame. Obtain the reading by turning the transmittance dial until the galvanometer needle is at zero. After every six to eight determinations of unknown samples, adjust the instrument with a standard sample in the range of the unknowns.

Comments

Adjustments to be made and precautions to be taken before and during every determination:

(1) Oxygen pressure, 10 p.s.i.

(2) Hydrogen pressure, 3 p.s.i. A change in pressure, as indicated by the width of the hydrogen pressure gage needle, is sufficient to give incorrect measurements.

(3) Dark current must be zero before and after each measurement. If not, measure again.

(4) Any yellowish tint to the flame usually indicates the presence of sodium.

Possible factors contributing to incorrect results are as follows:

(1) Phototube positioning switch not completely in or out.

(2) Plugged burner is usually indicated by aspiration continuing a short time after the solution is removed from the siphon tube. Also, the measurements are approximately the same value. Unplug the burner as follows: Turn off the hydrogen, leaving the oxygen on. Carefully push a wire (found with instrument) up the siphon tube;

never start from the top. If this does not solve the problem, the burner assembly may need repair and should be returned to the manufacturer.

(3) Slit width may have been accidentally changed.

Strontium by X–ray Fluorescence Emission Spectrometry

Equipment

(1) Mortar (agate) and pestle.
(2) Pipet—1 ml.
(3) Glass stirring rod.
(4) Spatula.
(5) Sample holder: Modified so that an aluminum alloy frame, 0.05 inch thick, can be slid into the holder and supported along the edges only. The center of the frame is cut out to match the opening in the holder. The bottom side of the frame is covered with 0.00025-inch Mylar film stretched tight and cemented to the frame with rubber cement. The irradiation beam is carefully centered so that no part of the holder or frame is irradiated.
(6) Microscope slide.
(7) Philips Norelco X-ray spectrograph, with FA–60 tungsten X-ray tube. The X-ray beam excites secondary X-rays from the sample. These are collimated to an analyzing crystal, then to a scintillation detector with linear amplifier and fast scaler. The X-ray tube is operated at 50 kv. and 40 ma.

Reagents

(1) Strontium standard solutions: From a stock solution (see reagents for Strontium by Flame Photometry) prepare dilutions containing 0, 20, 40, 60, 80, 100, 150, and 200 μg. of strontium per milliliter of solution.
(2) Ethyl alcohol (C_2H_5OH)—95 percent.

Procedure

Ash 100 g. of plant material, as described under Preparation of Samples. Record the weight of the ash and transfer the ash to an agate mortar, grind with a pestle, and mix to obtain a homogeneous mixture.

Prepare standard samples in an identical manner, except pipet 1 ml. of standard strontium solution (e.g., 0, 20, 40, 60, 80, 100, 150, and 200 μg. of strontium) into a mortar containing a slurry of 1 g. of ash and 20 ml. of 95-percent ethyl alcohol. Mix the slurry thoroughly with a glass stirring rod, dry overnight at 70° C., and mix thoroughly with mortar and pestle to obtain a homogeneous fine powder.

Transfer the powdered ash with a spatula to the aluminum alloy frame, backed with Mylar film, of the sample holder, level off with the edge of a glass microscope slide, and smooth with the flat side of the microscope slide to give a uniform surface for reflectance. About one-half gram of ash is required to fill the frame. It is not necessary to weigh definite amounts of the sample, nor is it desirable to pack the sample into the frame.

Place the filled frame in the sample irradiation chamber of the spectrograph. Scan the first sample of a series by setting the goniometer to run automatically over the desired range (about 20° or 30° 2θ) in order to obtain a picture of the area for a background and thus avoid choosing an angle for background with interference from other lines, up to the fifth order. The strontium Kα line appears at 25.15° 2θ, whereas the position of 25.90° is usually used for a background reading.

For quantitative analysis, use the peak-to-background ratio (P/B) of intensities as a measure of the strontium concentration. Obtain this ratio by setting the goniometer at 25.15° and recording the time necessary to measure 51,200 counts, then setting the goniometer at the background position (25.90°) and recording the time required for 51,200 counts. Convert the recorded times to counts per second, and calculate the ratio of the counts per second at the strontium peak to the counts per second at the background position.

Prepare a standard curve from measurements of the P/B in samples with added strontium. On the scan that was made, draw a straight line connecting the background on one side of the strontium peak to the background on the other side. Usually the background directly under the peak (25.15°) is higher than the one measured at 25.90°. This difference must be accounted for in determining the unknown amount of strontium originally present in the standard samples. The ratio of the count rate of the background at 25.15° to the count rate at 25.90° is called B/B. Subtract it from the P/B for the samples with added strontium. Then plot the net P/B versus the added strontium. Draw a straight line through the points and extrapolate to the negative X axis, which has the same scale as the positive X axis. This intercept gives the micrograms of strontium originally present.

Make a standard curve of the observed P/B to the total strontium (original plus added). Determine the strontium content of the unknown samples from their measured P/B in terms of micrograms of strontium per gram of ash. Multiply this by the weight of the ash and divide by the weight of the plant material to obtain the micrograms of strontium per gram of plant material.

The sensitivity for strontium is estimated to be between 2 and 3 p.p.m., and the error is estimated to be about plus or minus 8 percent.

Sodium and Potassium

Equipment

Flame photometer—D.U. Beckman model, with photomultiplier attachment and hydrogen-oxygen burner assembly.

Reagents

(1) Sodium standard solutions: Dissolve 2.542 g. of oven-dry reagent grade sodium chloride (NaCl) in distilled water and dilute to a volume of 1 liter. This stock solution contains 1,000 p.p.m. of sodium. Dilute appropriate volumes of stock solution with distilled water to prepare a series of solutions containing 0, 1, 2.5, 5, 10, 15, 20, 30, 40, and 50 p.p.m. of sodium.

(2) Potassium standard solutions: Dissolve 1.907 g. of oven-dry reagent grade potassium chloride (KCl) in distilled water and dilute to a volume of 1 liter. This stock solution contains 1,000 p.p.m. of potassium. Dilute appropriate volumes of stock solution with distilled water to prepare a series of solutions containing 0, 1, 2.5, 5, 10, 15, 20, 30, 40, and 50 p.p.m. of potassium.

Procedure

Sodium and potassium may be estimated by using the red or blue phototube. The settings for each tube are given in table 1.

TABLE 1.—*Settings for red and blue phototubes for estimating sodium and potassium*

Item	Red phototube		Blue phototube	
	Sodium	Potassium	Sodium	Potassium
Wavelength—mμ	587	767	587	767
Slit width—mm	15	0.04	0.02	0.05
Photomultiplier setting	Off	Off	2	Full
Resistor switch position	3	3	2	2

In all cases oxygen pressure is 10 p.s.i. and hydrogen pressure is 3 p.s.i.

In the U.S. Soils Laboratory the blue phototube is used and all procedures are the same as for strontium, except the settings given here.

DETERMINATIONS ON SEPARATE SAMPLES

pH of Soil

Equipment

(1) Beaker—50 ml.
(2) pH meter.
(3) Glass stirring rod.

Procedure (8)

To a 20-g. sample of soil in a 50-ml. beaker, add 20 ml. of distilled water and stir the suspension several times at regular intervals for about an hour. Measure the pH of the soil suspension with the glass electrode, stirring well just prior to immersing the electrode deep into the suspension.

Comments

Soil-water ratios ranging from 1 : 0.5 to 1 : 10 have been proposed for the determination of the pH of soils. The pH of most soils increases with dilution, usually attaining approximately a constant value at

1:5. There is little justification for using soil-water ratios wider than 1:1. The pH measurements of soils at a moisture content below that of the moisture equivalent are subject to several inherent errors and also make mandatory the use of a special glass electrode and pH meter.

Organic Matter Content of Soil

Equipment

(1) Erlenmeyer flask—500 ml.
(2) Burets—50- and 100-ml. dispensing burets for acid.
(3) Pipet—automatic 10 ml.
(4) Asbestos.
(5) Dropping bottle.

Reagents

(1) Potassium dichromate, 1 *N*: Dissolve 49.04 g. of reagent grade potassium dichromate ($K_2Cr_2O_7$) in water and dilute to a volume of 1 liter.

(2) Sulfuric acid (H_2SO_4)—not less than 96 percent.

(3) Phosphoric acid (H_3PO_4)—85 percent, U.S.P. grade.

(4) Barium diphenylaminesulfonate indicator: Prepare a 0.16-percent aqueous solution.

(5) Ferrous sulfate, 0.5 *N*: Dissolve 140 g. of reagent grade ferrous sulfate ($FeSO_4 \cdot 7H_2O$) in water, add 40 ml. of concentrated sulfuric acid (H_2SO_4), cool, and dilute to a volume of 1 liter. Standardize this reagent each day by titrating against 10 ml. of 1 *N* potassium dichromate, as given under Procedure.

Procedure (8)

Transfer a weighed quantity of soil (ground to pass a 0.5-mm. sieve), containing 10 to 25 mg. of organic carbon into a 500-ml. Erlenmeyer flask, and add 10 ml. of 1 *N* potassium dichromate. Then add rapidly 20 ml. of concentrated sulfuric acid from the 100-ml. dispensing buret, directing the stream into the solution. Immediately swirl vigorously by hand for 1 minute and let the flask stand on a sheet of asbestos for about 30 minutes. Then add 200 ml. of water, 10 ml. of phosphoric acid from the 50-ml. dispensing buret, and 10 drops of barium diphenylaminesulfonate indicator.

Proceed with the titration as follows: Add the ferrous sulfate until the solution is purple or blue, then add the ferrous sulfate in small amounts of about 0.5 ml. until the color flashes to green with little or no warning. Add 0.5 ml. of 1 *N* potassium dichromate to restore an excess of dichromate, and complete the titration by adding ferrous sulfate drop by drop to a light-green end point. If more than 8 ml. of the available 10 ml. of potassium dichromate is reduced, the determination should be repeated with less soil.

$$\text{Percentage of organic matter in soil sample} = \frac{(\text{milliliters of 1 } N \text{ potassium dichromate (reduced)})}{(\text{grams of sample})} \times 0.69$$

Comments

The estimation of soil organic matter based on the use of the conventional empirical factor for converting organic carbon to organic matter may be subject to considerable error, even when the organic carbon is determined accurately by the more tedious dry-combustion method. For this reason, the more rapid chromic acid-titration method is now widely used. Despite its simplicity, it has been shown to give results that agree closely with those obtained by the dry-combustion method when applied to a wide variety of soils.

In this method the soil is digested with a mixture of chromic and sulfuric acids making use of the heat of dilution of sulfuric acid. Consequently, it is necessary to add the sulfuric acid rapidly and to cool the flasks uniformly on a sheet of asbestos. The unpublished results of M. Peech indicate that the volume of the potassium dichromate solution and the concentrated sulfuric acid may be reduced to half that specified in the procedure without significantly affecting the results, provided, of course, that the size of the soil sample is proportionately reduced.

The color change of the optional *o*-phenanthroline indicator occurs at a much higher oxidation-reduction potential, and this indicator is theoretically superior to diphenylamine. With certain soils, however, the color change of diphenylamine is more easily observed than that of *o*-phenanthroline; hence, both indictors are recommended. The aqueous solution of barium diphenylaminesulfonate indicator is much more stable than that prepared by dissolving diphenylamine in concentrated sulfuric acid.

Nitrates interfere only if present in quantities in excess of 5 percent of the carbon content. Carbonates, even when they constitute 50 percent of the soil, do not affect the results. Since elemental carbon, as charcoal or coal, is practically unattacked in this method, this source of error is eliminated. Interference due to significant quantities of chlorides can be overcome by adding silver sulfate to the sulfuric acid, or a correction can be made if the quantity of chlorides is known. When chlorides are present in quantities less than the molecular equivalent of carbon, 1.25 g. of silver sulfate should be dissolved in each 100 ml. of concentrated sulfuric acid.

Exchangeable Hydrogen

Equipment

(1) Erlenmeyer flasks—125 and 250 ml.

(2) Gooch-type filter funnel—15 ml., 2-cm. diameter, coarse porosity (Corning, type 36060).

(3) Filter paper—glass-fiber or conventional paper (2.1-cm. diameter).

Reagents

(1) Buffer solution: Barium chloride ($BaCl_2 \cdot 2H_2O$), 0.5 *N*, and triethanolamine, 0.2 *N*: Dilute 100 ml. of commercial triethanolamine (specific gravity 1.126, about 8 *N*) with 1,000 ml. of distilled water and partially neutralize with hydrochloric acid (HCl) to

adjust to pH 8.1–8.2 (this requires approximately 360 ml. of 1 *N* hydrochloric acid). Make up to a volume of 2 liters with water and mix with 2 liters of a solution containing 250 g. of barium chloride. Protect from the carbon dioxide of the air.

(2) Replacement solution: Barium chloride: Dissolve 250 g. of barium chloride in 4 liters of distilled water, add 10 ml. of buffer solution, and mix.

(3) Sodium hydroxide, 0.01 *N*: This solution need only be approximate. Weigh 0.4 g. of sodium hydroxide (NaOH) and dissolve in 1 liter of distilled water.

(4) Bromcresol green, 0.04 percent: Triturate 0.1 g. of the indicator with 14.3 ml. of 0.01 *N* sodium hydroxide and dilute the mixture to a volume of 250 ml. with distilled water.

(5) Methyl red, 0.02 percent: Triturate 0.04 g. of the indicator with 1.5 ml. of 0.01 *N* sodium hydroxide and dilute to a volume of 200 ml. with distilled water.

(6) Standard hydrochloric acid, 0.10 *N*: Dilute 8.35 ml. of concentrated hydrochloric acid to a volume of 1 liter with distilled water. Standardize this solution against a standard base by accepted procedures.

Procedure (8)

Place 10 g. of soil in a 125-ml. Erlenmeyer flask, add 25 ml. of buffer solution, and allow the flask to stand for one-half hour, mixing the contents occasionally by swirling. Transfer to a Gooch-type filter funnel containing a moist filter paper disk and filter into a 250-ml. Erlenmeyer flask. Use an additional 25 ml. of buffer solution to aid in the transfer of all the soil to the funnel. Leach the soil with 100 ml. of the replacement solution by adding small increments. This filtration and leaching should not be completed in less than 30 minutes.

To the leachate, add 10 drops of bromcresol green and 2 drops of methyl red. Titrate with 0.10 *N* hydrochloric acid. The end point can be chosen as any point during the progressive color change from a bluish green through violet to pink. This end point should be checked against a blank containing 50 ml. of buffer solution and 100 ml. of replacement solution and titrated to the same end point with the 0.10 *N* hydrochloric acid. This end point should be reached when titrating the soil extracts. All calculations are made with this blank determination as a reference.

Available and Fixed Strontium 90 in Soils

Equipment

(1) Erlenmeyer flask—2 liters.
(2) Büchner funnels (6- and 8-inch diameter).
(3) Filter paper—Whatman No. 42 or equivalent.
(4) Suction flasks—1 and 2 liters.
(5) Beakers—150 and 800 ml., 2 and 3 liters.
(6) Hotplate.
(7) Funnel—long stem (9-cm. diameter).

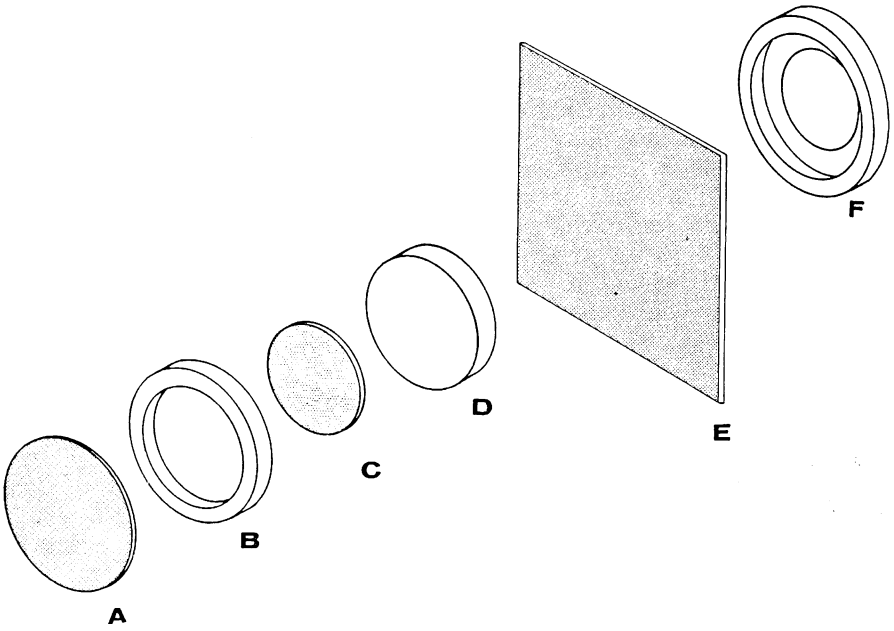

FIGURE 1.—Assembly of sample holder.

(8) Platinum evaporating dish—50 ml.
(9) Electric muffle furnace, with automatic temperature control.
(10) Mortar and pestle.
(11) Glass stirring rod.
(12) Indicator paper.
(13) pH meter.
(14) Ice bath—crushed ice in water.
(15) Mechanical stirrer.
(16) Glass wash bottle.
(17) Fritted glass filter assembly (see equipment for Strontium by Flame Photometry).
(18) Glass-fiber filter pad—2.1 cm.
(19) Sample holder (see fig. 1): Machine an aluminum disk 38 mm. in diameter and 4 mm. thick so that it has a 3-mm. well (wall thickness 3 mm.) and a hole in the center of the well 23 mm. in diameter (F). Make an aluminum ring (B) approximately 32-mm. outer diameter, 29-mm. inner diameter, and 3 mm. high so that it fits loosely in the well. Use a steel disk (D) 28 mm. in diameter and 3 mm. thick as backing for the sample. Assemble the parts as follows: Glue the Saran film (A) to the aluminum ring (B). Center the 2.1-cm. glass-fiber filter pad (C), on which the sample has been collected, on the steel disk (D). Place the aluminum ring (B) over the steel disk (D) so that the Saran film holds and protects the sample. Invert the ring (B) and the disk (D) and cover with the Saran film (E). Place the well of the machined aluminum disk (F) over the Saran film (E) and press down so that all other parts fit into the well. Trim any excess Saran film (E) with a sharp knife. The exact size of the sample holder may be varied to fit the automatic sample-changing equipment. The sample is then ready to count.
(20) Low-background G.M. counting equipment.

Reagents

(1) Strontium nitrate, 2 *N*: Dissolve 3,810 g. of strontium nitrate ($Sr(NO_3)_2$) in distilled water and dilute to a volume of 18 liters with distilled water.

(2) Hydrochloric acid: For 6, 2, 1, and 0.2 *N*, dilute 9 and 3 liters and 1,500 and 42 ml., respectively, of concentrated hydrochloric acid (HCl), each one to a volume of 18 liters with distilled water.

(3) Nitric acid (HNO_3)—concentrated, reagent grade.

(4) Yttrium carrier: Dissolve 4 g. of yttrium oxide (Y_2O_3) in 5 ml. of concentrated nitric acid. After the reaction is complete, dilute to a volume of 200 ml. Check the radioactive purity of this reagent. Add 1 ml. of reagent solution to 200 ml. of distilled water, add 5 ml. of concentrated nitric acid, allow to stand for 14 days, and milk as given under Procedure. If contaminated, the yttrium nitrate solution can be purified by following the procedures used in the Health and Safety Laboratory (*6*).

(5) Sulfuric acid (H_2SO_4)—concentrated, reagent grade.

(6) Sodium carbonate (Na_2CO_3)—reagent grade.

(7) Ammonium hydroxide, 4 *N*: Dilute 670 ml. of concentrated ammonium hydroxide (NH_4OH) to a volume of 2,500 ml. with distilled water. Ammonium hydroxide, 1 percent: Dilute 180 ml. of concentrated ammonium hydroxide to a volume of 18 liters with distilled water.

(8) Acetic acid, glacial (HOAc).

(9) Sodium dichromate, 1 *M*: Dissolve 298 g. of sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$) in water and dilute to a volume of 1 liter.

(10) Barium chloride, 0.5 *M*: Dissolve 61 g. of barium chloride ($BaCl_2 \cdot 2H_2O$) in water and dilute to a volume of 500 ml.

(11) Potassium cyanate (KCNO)—reagent grade.

(12) Ammonium oxalate: Add approximately 50 g. of ammonium oxalate ($(NH_4)_2C_2O_4 \cdot H_2O$) to 1 liter of water. An excess of salt should remain on the bottom after equilibrium is obtained by frequent shaking.

(13) Ethyl alcohol (C_2H_5OH)—95 percent.

(14) Standard strontium 90: Radioactive solution standard type RS 90 obtained from Nuclear Chicago Corporation, Standards Section.

(15) Potassium chloride (KCl)—reagent grade.

Procedure

Extraction of Soil.—Place 1 kg. of soil in a 2-liter Erlenmeyer flask with 1 liter of strontium nitrate solution. The concentration of strontium nitrate is adjusted so that 3 liters of it contains strontium equivalent to 10 times the total exchangeable cations of the soil, which were previously determined by the ammonium acetate method for bases and the barium chloride-triethanolamine method for hydrogen (p. 16). The strontium nitrate solution is easily made up for each sample from a stock solution of 2 *N* strontium nitrate. Stir the soil and solution well and allow to stand overnight. Filter through an 8-inch Büchner funnel, using Whatman No. 42 paper, into a 2-liter suction flask. After the soil has drained, resuspend it in 1 liter of the strontium nitrate solution for that soil, and filter again after 2 to 6 hours. This time the filtration will be much slower, and the sample may be divided about equally between two Büchner funnels. Wash the soil

with the third 1-liter part of the strontium nitrate solution. Combine the extracts in a 3-liter beaker and evaporate to dryness on a hotplate. These extracts contain the available fraction of the strontium 90.

Place the extracted soil in a 3-liter beaker and add 1.5 liters of 6 *N* hydrochloric acid. Stir well and allow to stand for 5 days on a hotplate at 70° to 80° C. Filter through an 8-inch Büchner funnel, washing with 1 liter of 1 *N* hydrochloric acid. Combine the extracts in a 3-liter beaker and evaporate to dryness on a hotplate. This material contains the fixed fraction of strontium 90. Discard the extracted soil.

Treatment of Extracts.—The small amount of organic matter in the strontium nitrate extract can be destroyed easily by adding 100 ml. of concentrated hydrochloric acid and evaporating to dryness. Dissolve the sample in 500 ml. of water containing 5 ml. of concentrated nitric acid and filter through Whatman No. 42 paper into an 800-ml. beaker. Add 1 ml. of yttrium nitrate solution containing 20 mg. of yttrium. The sample is now ready for removal of natural radioactive contaminants.

If the soil sample contained approximately 200 meq. or greater of calcium and magnesium, the strontium nitrate extract will need to be carried through the strontium sulfate precipitation procedure as described below for the hydrochloric acid extract. The large amount of strontium present will require splitting the sample to attain complete strontium precipitation. To check this, more sulfuric acid may be added to the filtrate to see if additional strontium sulfate forms. The strontium sulfate from all subsamples is combined for the fusing process.

The hydrochloric acid extract contains large quantities of aluminum, iron, silicon, and organic matter, as well as the desired strontium, and requires the following treatment: Add 100 ml. of concentrated nitric acid. After the reaction has subsided, begin heating gently to avoid loss of the foaming sample. Evaporate the solution to dryness. Dissolve the precipitate in 200 ml. of 6 *N* hydrochloric acid, heating as necessary. Dilute with 400 ml. of water and filter through a 6-inch Büchner funnel into a 1-liter suction flask. Transfer the filtrate into a 2-liter beaker and add 50 ml. of concentrated sulfuric acid to precipitate the strontium sulfate. Digest the precipitate on the hotplate for several hours, and filter through a long-stem funnel with Whatman No. 42 filter paper.

Transfer the paper and precipitate to a platinum evaporating dish and burn off the filter paper in a muffle furnace with the door open and temperature about 200° C. After the filter paper is charred, close the door and increase the temperature to 500° for 1 hour. Weigh the strontium sulfate and mix thoroughly with an equal weight of sodium carbonate, using a mortar and pestle. Place the mixture in a platinum evaporating dish and fuse it in a muffle furnace at 900°. After 1 hour at this temperature, turn off the furnace and allow the dish to cool inside the furnace. The cake then comes easily out of the dish. Place it in a 800-ml. beaker with 400 ml. of water, heat gently, and break up the cake with a glass stirring rod. When the cake is completely broken up, an undissolved residue of strontium carbonate remains. Filter through Whatman No. 42 filter paper in a 9-cm. funnel. Dissolve the strontium carbonate in 200 ml. of 2 *N* hydro-

chloric acid, and remove the small undissolved residue by filtration through Whatman No. 42 paper in a 9-cm. funnel. Add 1 ml. of yttrium nitrate solution containing 20 mg. of yttrium.

Removal of Natural Radioactive Contaminants.—Some soils contain radioactive contaminants that interfere with the determination of strontium 90, particularly in the hydrochloric acid extract. These are principally daughters of radium 226 and thorium 232. Scavenges with yttrium hydroxide and barium chromate remove most of the contaminants. The barium chromate scavenge is done by the method of homogeneous precipitation (*5*).

Heat the extracts and precipitate yttrium hydroxide by adding 4 *N* ammonium hydroxide to pH 8, using either indicator paper or a pH meter to check the pH. Digest the samples for 1 hour after the precipitate is formed. The precipitate often contains noticeable quantities of manganese oxide, ferric hydroxide, and aluminum hydroxide. Filter through Whatman No. 42 paper in a 9-cm. long-stem funnel, maintaining a column of liquid in the funnel stem to speed the filtration.

For the barium chromate scavenge, acidify the filtrate with 5 ml. of concentrated nitric acid and add 1 ml. of acetic acid, 1 ml. of 1 *M* sodium dichromate, and 2 ml. of 0.5 *M* barium chloride. Adjust the pH of the extracts to 2.0–2.5 by adding ammonium hydroxide. Cool the extracts in an ice bath while using a mechanical stirrer. Stir 3 g. of potassium cyanate, dissolved in a little water, into the extract. After 3 to 6 hours of continuous stirring and when the pH of the extract has risen to 5.0–5.2, filter through Whatman No. 42 paper and discard the precipitate. It is necessary to repeat the barium chromate scavenge at least once. Add 5 ml. of concentrated nitric acid, 1 ml. of 1 *M* sodium dichromate, 2 ml. of 0.5 *M* barium chloride, adjust the pH to 2.0–2.5, and proceed as for the first barium chromate scavenge. Add 5 ml. of concentrated nitric acid and 1 ml. of yttrium nitrate solution to the extracts and heat to remove the dissolved carbon dioxide. Proceed with the final yttrium hydroxide scavenge, as indicated in the preceding paragraph. Put aside the extracts for buildup and milking of yttrium 90.

Milking of Yttrium 90.—The yttrium 90 radioactive daughter of strontium 90 is easily separated from the large amount of strontium in the two extracts. Since yttrium 90 has a half-life of 64.6 hours, it reaches 97 percent of its equilibrium value with strontium 90 in 2 weeks after any separation. Thus, milkings can be made repeatedly. Each time the extracts are put aside for buildup of yttrium 90, they are acidified with concentrated nitric acid and 20 mg. of yttrium is added.

Heat the sample and precipitate yttrium hydroxide as for the yttrium hydroxide scavenge. After digestion and filtration, dissolve the yttrium hydroxide in a minimum quantity of hot 0.2 *N* hydrochloric acid, which is directed on the precipitate as a stream from a wash bottle. Collect the yttrium chloride solution in a 150-ml. beaker. Heat, add 5 ml. of saturated ammonium oxalate solution, and adjust the pH to 6.0. Allow the precipitated yttrium oxalate to digest about 1 hour. Then filter through a small fritted glass funnel, catching the precipitate on a 2.1-cm. glass-fiber filter pad. Dry the precipitate by washing with 95-percent ethyl alcohol. Transfer it to a sample holder (fig. 1) for the radioactivity determination.

The radioactivity determination is made with an end window G.M. tube. Use anticoincidence circuit and shielding to obtain background counts of 1.5 to 2.0 c.p.m.

Count the sample four times over a 2-week period. Two of these counts should be within the first 3 days after the yttrium hydroxide precipitation. Make the third count approximately 5 days after the precipitation and the final count after 10 days.

For each count a standard deviation is calculated according to the following equation:

$$\text{Standard deviation} = \frac{\sqrt{N_{\text{bkg.}} + N_{\text{sample}}}}{t}$$

Where $N_{\text{bkg.}}$ = total count of background in time (t)

N_{sample} = total count of sample in time (t)

The count per minute plus or minus its standard deviation is plotted against the theoretical fraction of yttrium 90 left. This fraction is determined from its radioactive decay constant. For example, one-half is left 65 hours after precipitation of yttrium hydroxide and one-fourth is left 130 hours after precipitation. The time interval for radioactive decay is taken as the midpoint of each of the four counting periods. If the sample is uncontaminated, a straight line will result, which intercepts the abscissa at zero, showing no yttrium 90 left. The extrapolated line to the ordinate becomes the disintegrations per minute of strontium 90 per original soil sample when the appropriate efficiency factor is used.

The efficiency factor is obtained by taking a solution containing a known amount of strontium 90 through the entire procedure. This factor should be rechecked every 2 months. Potassium chloride is used as a working standard. The weight of potassium chloride used is estimated from the count rate of the samples being analyzed. One gram of potassium is equivalent to 1,776 disintegrations per minute. The potassium chloride standard and background counts should be made every 2 days.

Strontium 90 in Plants

The strontium 90 determination for plant material is basically the same as described in the preceding section for soils. Strontium 90 is brought into solution, interfering ions are eliminated, and yttrium 90 is separated. The amount of plant material used will vary according to its strontium 90 content. With low-background counting equipment, 1 picocurie is about the minimum that can be determined accurately. Ten or more picocuries are desirable for a quicker and more accurate determination.

Several hundred grams of plant material are generally used to obtain high enough count rates for a convenient radioactivity determination. Thus, other ions may be sufficiently concentrated so as to cause interference with the chemical procedure. Phosphate and sulfate may interfere, but they can easily be removed by following the strontium

sulfate precipitation procedures given in the preceding section pertaining to the treatment of the hydrochloric acid (HCl) extract of soil. Calcium may interfere in the filtration of the strontium sulfate. In this case the supernate is decanted, while still hot, from the strontium sulfate precipitate. The supernate is filtered quickly and the material on the filter paper is recombined with the strontium sulfate.

The plant material may be contaminated with fresh fission products, which could interfere in the yttrium 90 radioactivity measurement. The interfering fission products can be eliminated by following the yttrium hydroxide and barium oxalate scavenge procedures described in the preceding section. The yttrium 90 milking procedure and radioactivity measurement are performed as given in the preceding section.

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