Experiment 12

Vegetation Sample Preparation for Radiochemical Analysis of Radio-strontium

Objective

To prepare a vegetation sample for radiochemical analysis.

Introduction

This laboratory experiment describes the preparation of a vegetation sample (e.g., grass) for radiochemical analysis. The sample is dried and ashed. In Part 12A, the ash is fused with sodium hydroxide and sodium carbonate to bring it into solution. An alternative method in Part 12B uses a microwave-assisted digestion technique with nitric and hydrofluoric acid. The prepared sample is suitable for radionuclide analysis, notably for radio-strontium or plutonium.

Proper preparation of biological solids for radiochemical analysis is essential for obtaining valid radioanalytical chemistry results. The samples often must be large because the radioactivity levels are low. Gamma-ray spectral analysis is the preferred method of radiation measurement because it requires little preparation. If gamma-ray spectral analysis of the untreated sample is not feasible because few or no gamma rays are emitted, the sample must be dissolved. Dissolution is almost always required for alpha- and beta-particle analysis. The first step usually reduces the mass of the solid sample and prepares it for dissolution.

Some types of collection provide a concentrated or reduced-volume sample directly. Examples include filtration to collect airborne or waterborne particles, and sorption of airborne gases on charcoal and of aqueous ions on ion exchange resins. Water samples are reduced in volume by evaporation, and organic solids, by ashing. Certain radionuclides in water are concentrated by precipitation.

Biota samples usually are processed by dissolution in strong oxidizing acids or by dry combustion. In combustion, carbonaceous matter is removed at elevated temperatures as carbon dioxide and water in the presence of oxygen (air). Alternatively, some materials may be macerated with enzymes or in basic solution. Whatever process is used, the most important point in selecting

a procedure is that the radionuclides of interest are quantitatively recovered in a soluble form.

The process for converting the vegetation sample to a soluble form is selected for convenience, familiarity, safety, and optimal removal of interfering substances. A problem in dissolving salts of heavier Group IIA elements with mineral acids is that they may be insoluble sulfates. The most common method for bringing insoluble sulfates into solution is to subject the sample to hydroxide-carbonate fusion (fusion is discussed in Section 4.6.2 of your *Radioanalytical Chemistry* text). The fusion is performed in a metal crucible that is relatively insoluble under the fusion conditions. The temperature must be sufficiently high to melt the sulfates and convert them into carbonates. The carbonates are then dissolved to prepare the sample for analysis.

Preparation of a vegetation sample for radiochemical analysis in this procedure requires three steps. In the first, the sample is dried at 105°C. In the second, the dry material is ashed at 550°C to remove the carbonaceous material. In the third step, either fusion or microwave-oven dissolution brings the salts into solution.

Safety Reminders

- Follow the usual safety procedures when working in a radiological laboratory.
- Carefully handle very hot containers, fusion mixtures and samples from muffle furnaces.
- Caution should be exercised when preparing and working with corrosive mineral acids.
- All liquids/solids are to be properly disposed of according to laboratory rules and protocol.
- Perchloric acid is effective in dissolving certain solids but is not used here because it poses an explosion hazard, notably with carbon. The acid should only be used to dissolve carbon-containing materials where perchloric acid hoods are available and the chemist is fully trained and certified to work with perchloric acid for this purpose.

Equipment and Supplies

- Scales
- Nickel crucible, 125-mL or 250-mL size
- Nickel stirring rod
- Tongs
- Ice bath
- 50-mL centrifuge tubes
- Fine-porosity filter paper and filtering funnel
- Reagent bottles
- Drying pans, large, but suitable for oven volume
- Porcelain ashing dishes, large, but suitable for muffle furnace volume
- Pipettes, 1 and 4 mL

Reagents (for fusion of ash)

- Vegetation sample: grass or other suitable plant material, at least 250 g
- Strontium carrier, standardized, 10 mg Sr^{+2}/mL: see Experiment 5

- Barium carrier, ~10 mg Ba^{+2}/mL: Dissolve 9.5 g of $Ba(NO_3)_2$ in 200 mL of deionized water and dilute to 500 mL.
- 2 M calcium nitrate: Dissolve 236 g of reagent grade $Ca(NO_3)_2.4H_2O$ in 200 mL of deionized water and dilute to 500 mL.
- Sodium hydroxide pellets, reagent grade
- Sodium carbonate, solid, reagent grade
- Concentrated HNO_3
- 6 M HCl (Pour 500 mL of concentrated HCl carefully into ~400 mL deionized water, stir and dilute to 1 L with deionized water.
- Deionized water

12A. Drying, Ashing, and Fusion

Procedure

Sample ashing

Step 1. Weigh approximately 250 g of a fresh vegetation sample, such as grass. Record its moist weight in Data Table 12.1.

Step 2. Transfer the vegetation to a flat drying dish or pan. Dry overnight in an oven at 105°C. Remove the sample from the oven and let it cool to room temperature. Record the dried weight to nearest 0.1 g in Data Table 12.1. If the sample weighs more than 120 g, record the weight and calculate the dry-to-moist weight ratio. Then remove the vegetation in excess of 120 g, weigh the remaining sample, and record its weight in Data Table 12.1 for comparison with its ash weight.

Step 3. Place vegetation sample in several large porcelain dishes, one of which is tared. Gradually heat sample in open muffle furnace while dish is covered (with small opening to admit air) to char sample. Close furnace, increase the temperature to 550°C and ash overnight. Remove the porcelain dishes from the furnace. Remove the cover and mix ash with stirring rod. If black particles remain in the ash, return the porcelain dishes, partially covered with lid to admit air, to furnace, and close door. Ash the sample overnight again at 550°C. Remove the sample from furnace and let it cool to room temperature. Combine all ash samples in the tared porcelain dish. Weigh the porcelain with its contents. Record the ash weight in Data Table 12.1 and calculate the ratio of ash-to-dried weight relative to the near-120-g sample.

Sample fusion method

Step 4. Place 5.00 g of ash in a 125-mL or 250-mL nickel crucible. *Note: the type of crucible is selected that is relatively stable for the fusion temperature and mixture. Platinum crucibles are more stable but also more costly.* See

Data Table 12.1 Sample weight

1.	Weight of Fresh Vegetation
2.	Dried Weight
3.	Dry-to-Moist Ratio (Steps 2./1.)
4.	Weight of Dried Sample Used
5.	Ashed Weight
6.	Ash-to-Dried Ratio (Steps 5/4)

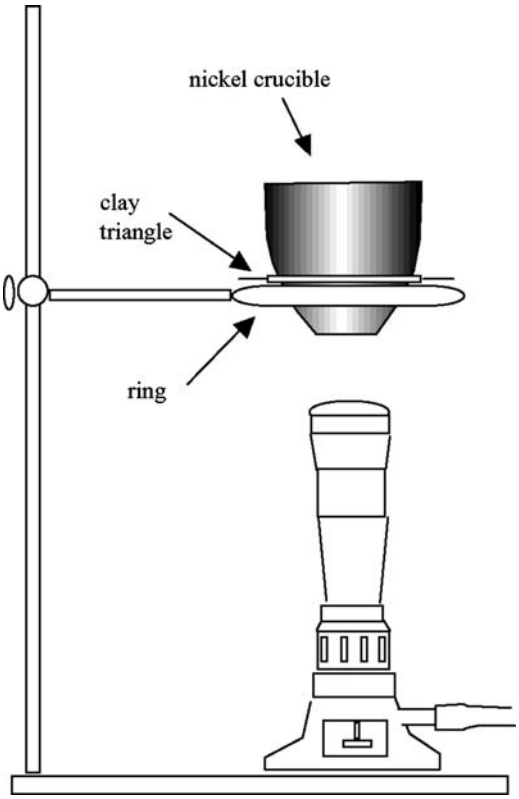

Figure 12.1 Arrangement for nickel crucible fusion.

Figures 12.1 and 12.2 for the fusion arrangement. Pipette 4 mL of strontium carrier and 1 mL of barium carrier onto the sample. Add 1 mL of 2 M $Ca(NO_3)_2$ solution. Add 25 g of NaOH pellets. Carefully heat over Meeker burner for 30 minutes. Remove from heat and slowly add 2.5 g of Na_2CO_3 to the hot melt, stir with nickel stirring rod, and continue heating the clear melt for 30 minutes to convert calcium, strontium, barium, and radium salts to carbonates.

Step 5. Transfer the crucible from the flame directly to a cold-water bath to crack the melt. *(Caution: the hot crucible in contact with water produces steam and possible splattering.)* Add 100 mL deionized water to the melt in the crucible. Boil gently over the flame to disintegrate the fused mixture.

Step 6. Cool the crucible in the ice bath. Slurry most of the solid and solution into two 50 mL glass centrifuge tubes. Balance the tubes and centrifuge them at full speed for approximately 1 minute. If the supernate is cloudy after centrifugation, centrifuge again until it is clear. Discard the supernatant solution by carefully pouring the supernatant into a beaker. Add the remaining contents of the crucible to the centrifuge tubes. Balance the tubes. Repeat the centrifugation. Discard the supernate as before. Use 80 mL of deionized water in several fractions to rinse the crucible and add the wash water to the two centrifuge tubes that contain the solids. Stir the solids vigorously in water. Repeat the centrifugation. Discard the supernate.

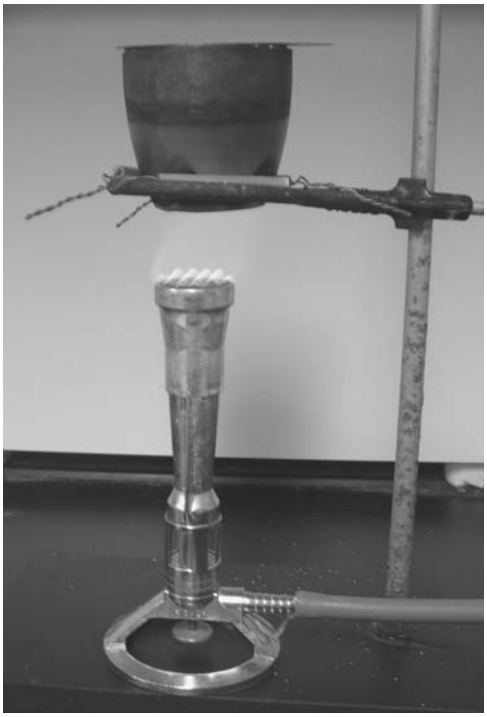

Figure 12.2 Fusion apparatus.

Step 7. Dissolve the solid carbonates in 20 mL of 6 M HCl (10 mL per tube) by boiling gently with constant stirring. (Use caution: the sample can be lost if the analyst has not practiced boiling in centrifuge tubes). Add 30 mL deionized water to each tube. Pour the contents of both tubes through a funnel fitted with a filter paper into a clean 500-mL bottle that is fitted with a cap. Wash the tubes and the filter paper with 240 mL of deionized water in several portions; add the wash water to the filtrate in the bottle. Discard the filter paper with any insoluble silicates.

Step 8. Mix the dissolved sample. Measure its volume and record it. Relate the initial dried sample weight to this volume. Close the bottle, label its content, and save the solution for the determination of radio-strontium (Experiment 13).

Sample volume:_____

Ratio of dried sample weight to volume:____

12B. Drying, Ashing, and Acid Dissolution

Procedure

Steps. 1 – 3. Follow Steps 1 – 3 from Part 12A (above).

In this alternative, a 1- or 3-g sample aliquot is treated by microwave-assisted dissolution according to the method by Garcia and Kahn cited following this procedure.

Step 4a. For *microwave-assisted digestion*, follow the procedure developed for the microwave system in the laboratory. Note that total dissolution of the solid is required for radioanalytical chemistry, whereas partial dissolution is acceptable for other analytical processes if the method has been tested for fractional recovery. Several references are given below that may be helpful in developing or using this method.

Step 4b. For *leaching* a vegetation ash sample, strong mineral acids such as HNO_3 can be used. *Note: A leach recovery fraction must be determined that applies specifically to the matrix*, *radioanalyte*, *leaching solution*, *and leaching program (temperature*, *relative volumes*, *time) under consideration*.

Questions

1. Why is it important to record the weights of the vegetation both as a wet weight and a dry weight?
2. If part of the sample were lost during the dissolution of the melt cake in Step 7, how would this affect your final results? Explain.
3. If the sample had an unusually high amount of silicates, what could you do to remedy the excess silicate problem?
4. What happens when strong sodium hydroxide solutions come in contact with glass?
5. Look up a procedure that uses only a wet ash method. Which do you think is better? Why?
6. Why is it not necessary to standardize the barium carrier and the calcium solution?

Source for Part 12A

Adapted from a procedure used at the Environmental Radiation Branch, GTRI, Georgia Institute of Technology, Atlanta, GA.

Sources for Part 12B

H.M. Kingston, ed., and S.J. Haswell, ed., Microwave-Enhanced Chemistry, 772 p, American Chemical Society, Washington, DC (1997).

David Barclay, "Microwave Digestion Moves into the 21st Century," Today's Chemist at Work, pp 28–32 March 2004; www.tcawonline.org

R. Garcia and B. Kahn, "Total Dissolution of Environmental and Biological Samples by Closed-Vessel Microwave Digestion for Radiometric Analysis," J. Radioanalytical and Nuclear Chemistry **250**, 85–91 (2001).

J.S. Alvarado, T.J. Neal, L.L. Smith and M.D. Erickson, "Microwave Dissolution of Plant Tissue and the Subsequent Determination of Trace Lanthanide and Actinide Elements by Inductively Coupled Plasma-Mass Spectrometry," Analytica Chimica Acta **322**, 11–20 (1996).