



Techniques of Water-Resources Investigations of the United States Geological Survey

Chapter A5

METHODS FOR DETERMINATION OF RADIOACTIVE SUBSTANCES IN WATER AND FLUVIAL SEDIMENTS

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**Book 5
LABORATORY ANALYSIS**

Tritium

Liquid scintillation method, Reston lab (R-1173-76)

Parameters and codes: Tritium, dissolved (pCi/l): 07005
Tritium, in water molecules (Tu): 07012

1. Application

The technique can be used directly to analyze waters containing more than 60 Tu (190 pCi/l). Many natural-water samples contain less than 60 Tu so the tritium in such samples is normally enriched by electrolysis (method R-1174-76) before they are analyzed by this technique.

The direct liquid scintillation counting method, while useful for analysis of the tritium introduced into water by rainout in some samples, is primarily used for measuring tritium introduced in tracer tests and locally by nuclear power and waste disposal facilities.

2. Summary of method

Liquid scintillation counting is based on the conversion of the energy of a particle emitted by a radioactive nucleus to light energy by means of a scintillating chemical. The scintillations are detected by a photomultiplier (PM) tube. The electrical signals from the PM tube are amplified and sent through a two or three channel analyzer where sorting by energy ranges takes place. The counts in each channel are displayed on a scaler and are printed and (or) read out on punched tape or magnetic tape. In order to minimize spurious counts, from cosmic radiation or electrical noise inherent in the PM tubes themselves, for example, two PM tubes are used to detect the scintillations. The two tubes are operated in coincidence, so that only if a scintillation event is detected by both tubes simultaneously is a signal sent

on to the energy analyzer and scalar circuitry.

When liquid scintillation counting is used to determine a radionuclide in aqueous solution, the water sample is dissolved or dispersed in a larger volume of organic solvent containing the scintillating chemical. A widely used mixture for aqueous solutions was dioxane-naphthalene containing the scintillator 2,5-diphenyloxazole (PPO) and a secondary scintillator used to shift the wavelength of the scintillations to the most sensitive spectral region of the PM tube. Much early tritium data was determined by use of the above scintillation mixture. The dioxane-PPO combination has been superseded by proprietary scintillators that produce gels when mixed with water in proper ratios. The newer scintillators have approximately doubled the sensitivity of liquid scintillation counting for tritium. These solutions generally include an organic solvent (toluene or xylene, for example) in which the scintillator is dissolved, plus a strong liquid detergent to promote emulsification between the sample water and the scintillator-containing organic solvent.

Since the exact composition of the proprietary mixtures is not available, these are listed by trade name in the reagent section.

While the mechanism of liquid scintillation counting is not completely understood, it seems clear that the energy transfer is a two-stage process, with initial energy transfer to the solvent followed by transfer from the solvent to the scintillator. Many

substances, including water, interfere in the energy transfer process to quench the scintillations and reduce the count rate. Excessive salt content, certain metals, and organic compounds quench in varying degree. Colored substances may quench by light absorption in addition to interfering with energy transfer. Quenching substances are generally removed by vacuum distillation.

The quenching effect of water is compensated by using a constant volume of water and constant ratio of water sample to scintillator mixture in both samples and standards. The count rate of a particular sample depends on both the volume of sample and the ratio of liquid scintillator mixture to water sample. As the fraction of water sample in the water scintillator mixture increases, count rates increase until a point is reached where the quenching effect of the additional tritiated water exceeds the effect of the increased radioactivity. It is found that a practical compromise between maximum sample volume and scintillator volume provides optimum sensitivity. The ratio of sample to scintillator solution (in a constant total volume) can vary slightly without affecting the counting characteristics of the mix. Thus optimally sensitive mixes can be produced in routine work.

The permissible ratio of water sample to liquid scintillator mix is also controlled by physical stability of the gel formed. A detailed description of the method is given by Schroder (1971), and the counting characteristics and thermal stability of various water-scintillator solution mixtures are given in the manufacturers' literature.

3. Interferences

Potential interferences come from other radionuclides or quenching substances present in the sample. Both types are removed by vacuum distillation of the sample before preparation of the counting mixture.

A rare ground-water sample may contain radon-222 in an amount large enough to persist in the sample even after distillation. Some radon decay is counted in the tritium energy channel and leads to spuriously high

results. Radon has a short half-life (3.8 d) and its presence is obvious from a decline in count rate while a sample is counted over a period of several days or a week.

A radon-containing sample can be purified by distilling it to remove any parent radium-226, allowing the sample to stand for 3-4 weeks for the radon to decay, and redistilling before counting to remove the radon daughter lead-210.

The analysis of tritium in highly radioactive samples, such as those from nuclear facilities, may be confused by the presence of other radioactive noble gases, particularly krypton-85 and argon-41. Rhinehammer and Lamberger (1973) discuss techniques for tritium analysis in the presence of concentration of other radioisotopes much higher than found in natural samples.

Samples prepared for counting by electrolytic enrichment are normally free of radioactive or quenching interfering substances.

4. Apparatus

4.1 *Counting equipment*, liquid scintillation spectrometer, with two PM tubes, operating in coincidence minimum of two channels for pulse-energy analysis; automatic sample changer, minimum 100 samples; constant temperature chamber for PM tubes and shield and sample changer, adjustable to as low as 0°C; readout device(s) to paper for visual inspection of results and to punched tape or other automatic data processing (ADP) compatible form for data transfer to computer for final calculations. Optional: automatic external standardization by channels-ratio method for quench determination. Properly prepared samples do not differ in quenching, and this determination is unnecessary. The presence of the external standard source near the counting chamber may add additional background.

Counters as received from the manufacturer will not normally be adjusted for optimum counting of water mixtures, and before routine tritium measurements are begun must be carefully adjusted in the laboratory

gun. Adjustments are possible to: PM-tube high voltage; amplifier gain; energy analyzing channel limits; and (by a manufacturer's representative) the time interval in which a pulse in one PM tube is taken as simultaneous with a pulse in the other and sent on to the analyzer circuitry.

The type of scintillator solution and optimum water to solution ratio of the counted mixture must also be chosen, and the counting-chamber temperature set as low as possible to minimize PM-tube noise without causing the counted mixture to separate or freeze.

The utility of a liquid scintillation spectrometer for low-level counting is determined by its background count rate and its tritium-counting efficiency. A frequently used counting mixture consists of 12 ml H₂O sample plus 13 ml Insta-Gel (Packard Instrument Co.), in a polyethylene vial. Presently available (1976) commercial counters are capable of counting this mixture, with efficiencies of 20 percent or greater, and backgrounds of 3.6 cpm or less. Older instruments, with efficiencies as low as 12 percent and backgrounds as high as 3.8 cpm, may also be satisfactory, but will require longer counting times.

4.2 *Counting vials*, commercial, screw-cap polyethylene liquid scintillation counting vials, with caps with reflective liners.

4.3 *Vacuum-distillation apparatus*.

4.4 *Miscellaneous glassware*, pipets for preparing counting mixtures, standard solutions, and so forth.

4.5 *Analytical balance*.

5. Reagents

5.1 *Scintillator*, commercial solutions for counting water mixtures, such as: Insta-Gel, Packard Instrument Co.; Ready-Soln, Beckman Instrument Co.; Scintillator 3A70*, Research Products International; Scinti Verse, Fisher Scientific Co.; Aquasol, Nuclear Associates; or ScintillAR, Malinkrodt Chemical Co.

5.2 *Tritium standard solution*: Appropriate standards for determining counter efficiency are prepared by the dilution of NBS

standard tritiated water with "dead" water, that is, water containing less than 1 Tu. A standard containing 50 to 100 dpm/ml tritium (7 to 15×10^3 Tu) is adequate.

5.3 *Water, "dead"*. Water with no measurable tritium ("dead" water) is required for determination of counter-background rate and for dilution of standard tritiated water. It is very difficult to confirm that a water is truly "dead," and it is usually necessary to make the assumption that water from a deep well in a confined aquifer a hundred kilometers or more from the recharge area is "dead." This assumption can be correct only if the well is pumped sufficiently to expel all meteoric water that may have entered the well and surrounding aquifer by leakage.

6. Procedure

6.1 *Distillation*. Samples enriched by electrolysis are distilled in the final step of that procedure and require no further treatment before preparing the counting mixture. All other samples must be vacuum distilled before preparing the counting mixture.

6.2 *Counting*. Samples are counted in sets, each requiring about 1 week of counting. A set typically includes 1 standard, 1 or 2 blanks (backgrounds), and from 7 to 15 samples. The number of samples per set depends on tritium content. Low-tritium samples require longer counting times, and so fewer can be counted per week.

Members of a count set are prepared together and in the same way. The proper volumes of sample, standard, or "dead" water is pipetted into a tared counting vial and its mass determined to ± 0.01 g. The scintillation solution is then added by manual or autopipet. The water to scintillator solution ratio must be constant within a count set for the optimized counter settings. If sufficient sample volume is not available, following electrolysis, for example, the mass of sample in the counting vial is first measured, then "dead" water added to bring the total water volume to that required by the counter settings.

The vials are capped and the contents thoroughly mixed. Heating the mixture to

40°–60°C promotes emulsification, but is not necessary. The set is then placed in the counter sample changer for at least 24 hr before counting begins to reach thermal equilibrium and for chemiluminescence (if any) to decay.

Members of each set are counted sequentially for a preset time (40 to 100 min) or until a preset number of counts (5,000 to 10,000) have accumulated. The counter then records the sample number, count time, and counts accumulated, and moves the next sample into position. After the last sample, the sample changer returns to the first sample and the cycle repeats.

If the automatic external-standardization option on the counter is used, the standardization is done at the end of each count on each sample and the results recorded before changing to the next sample.

The total time required for counting a sample is determined by its tritium content (see sec. 7.3 below). If a set contains several high-tritium samples, these can be removed individually when they have counted long enough, and counting of the remainder of the set continued.

7. Calculations

7.1 Tritium counting efficiency (E). Use equation 2:

$$E = \frac{\bar{c}_n}{d_n (e^{-\lambda t_n}) \times V_n}, \quad (2)$$

where

\bar{c}_n = average count rate of standard (cpm) above background ($\bar{S} - \bar{B}$),

d_n = disintegration rate of standard (dpm/g),

V_n = mass of standard counted (g),

λ = decay constant of tritium ($1.534 \times 10^{-4} \text{ d}^{-1}$),

t_n = elapsed time between certification of the standard and time of count in same units as λ ,

where

\bar{S} = average count rate (cpm) of the standard in the set, and

\bar{B} = average count rate (cpm) of the blank(s), (backgrounds) in the set.

7.2 Calculation of tritium concentration. Use equation 1:

$$Tu = \frac{\bar{C}}{KVEf (e^{-\lambda t})}, \quad (1)$$

where

\bar{C} = average sample count rate above background (cpm),

V = mass of sample water counted (g),

E = counting efficiency, from equation 2,

$$\left[\frac{\text{cpm}}{\text{dpm}} \right],$$

f = electrolysis enrichment factor. For samples counted directly, $f=1$ (for calculations of f for electrolyzed samples, see method R-1174-76),

λ = decay constant of tritium ($1.534 \times 10^{-4} \text{ d}^{-1}$),

t = time elapsed between sample collection date and date counted, in same units as λ , and

$K = 7.13 \times 10^{-3} \text{ dpm/g Tu}$.

7.3 Calculation of tritium counting error.

The error term which accompanies tritium results is calculated such that there is a 67 percent probability that the true tritium content of the sample is in the range of the reported value \pm the error term.

Errors of tritium analyses are due primarily to the uncertainty inherent in any attempt to measure the rate of occurrence (count rate) of a random process (radioactive decay). For a count rate, R , the standard deviation $\sigma = R/t$, where t is the total count time. Errors in counting both the sample and background are included in the net sample count rate \bar{C} , above. That is, if $\bar{C} = \bar{S} - \bar{B}$,

$$\sigma \bar{C} = \sqrt{\sigma_{\bar{S}}^2 + \sigma_{\bar{B}}^2}. \quad (3)$$

In sets counted as described above, the counting time for background and sample are the same, so equation 3 can be written:

$$\sigma \bar{C} = \sqrt{(\bar{C} + 2\bar{B})/t}. \quad (4)$$

The relative error, or precision of the count rate measurement is:

$$\sigma_{\bar{C}}/\bar{C}.$$

Thus equation 4 shows that analytical precision increases ($\sigma_{\bar{C}}/\bar{C}$ becomes smaller) with longer count time, or, for a fixed count time, increases with higher sample count rates (a higher tritium-counting efficiency or a higher sample tritium concentration) or with a lower background count rate.

In addition to the count-rate error, small errors are associated with each of the other terms in equation 1, and the reported σ_{Tu} is calculated with the expression

$$\sigma_{Tu} = Tu \times \sqrt{\left(\frac{\sigma_{\bar{C}}}{\bar{C}}\right)^2 + \left(\frac{\sigma_{\nu}}{\nu}\right)^2 + \left(\frac{\sigma_E}{E}\right)^2 + \left(\frac{\sigma_f}{f}\right)^2} \quad (5)$$

There are also errors associated with the K and $(e^{-\lambda t})$ terms in equation 1, primarily due to uncertainties in the knowledge of the tritium half-life, but they are negligible for most purposes.

Because Tu-error calculations are tedious and complicated, they are done by computer from the counting data punched or otherwise directly recorded by the counter.

8. Report

Tritium errors are reported to two significant figures or to the nearest 0.1 Tu, whichever is larger. The tritium result itself is reported to the same number of significant figures.

Tritium data are frequently required in pCi/l rather than in Tu. To convert, use the expression:

$$\text{pCi tritium/l} = 3.2 \text{ Tu.}$$

9. Precision

The precision of tritium analyses varies with sample tritium content and with laboratory configuration and location. The one standard deviation (1σ) error is reported with each result. The calculation of this error is described above (sec. 7.3).

References

- Schroder, L. J., 1971, Determination of tritium in water by the U.S. Geological Survey, Denver, Colo.; U.S. Geol. Survey Rept. USGS-474-134, 22 p.; Avail. *only* from U.S. Dept. Commerce, Natl. Tech. Inf. Service, Springfield, VA. 22151.
- Rhinehammer, T. B., and Lamberger, P. H., 1973, tritium content technology, U.S.A.E.C. report WASH-1269, 292 pp. (Avail. from NTIS).

Tritium

Electrolytic enrichment—liquid scintillation method, Denver lab (R-1172-76)

Parameters and codes: Tritium, dissolved, (pCi/l): 07005
Tritium, in water molecules (Tu): 07012

1. Application

Gas counting preceded by electrolytic enrichment is the most sensitive analytical method for tritium and is applicable down to concentrations in the range of 1 Tu. With very careful control of ambient laboratory tritium levels, and a valid blank based on "dead" water, it is possible to apply the method to waters as low as 0.2 Tu. Where gas-counting equipment is not available or where a lower detection limit of 25 Tu is satisfactory, electrolytic enrichment followed by liquid scintillation counting permits the analysis at lower concentrations than by liquid scintillation alone (method R-1171-76). The technique also may be applied to samples having high concentrations of nonvolatile radioactivity contamination such as strontium-90, because the sample preparation steps eliminate solid materials.

The technique is generally applicable to determine tritium introduced into water by rainout and to measure natural levels of tritium in surface waters. The technique is not sufficiently sensitive for the determination of very low natural tritium levels.

2. Summary of method

When it is necessary to determine tritium at a lower concentration, with improved accuracy, than is available in the liquid scintillation method (R-1171-76), an electrolytic enrichment step is introduced ahead of the liquid scintillation counting. The electrolysis

techniques were introduced by Kaufmann and Libby (1954).

Electrolytic enrichment is carried out by adding sodium peroxide (forms sodium hydroxide), followed by carefully controlled electrolysis in specially designed cells. The cells of Östlund and Werner (1961) are used. The isotopic fractionation factors are improved by operation at low temperature. Hence, the electrolysis is carried out while the cells are partially immersed in a cold bath maintained at a temperature just above freezing.

The percentage of recovery of tritium in the electrolysis is a complex function of temperature, current density, and electrode surface reactions which are not fully understood. Practical systems have been developed which achieve 70-80 percent recovery of tritium in electrolysis from approximately 500 to 10 ml. More extensive electrolysis provides greater enrichment but lower percentage of recovery. The reproducibility of recovery between electrolyses is approximately 3-4 percent under normal conditions.

Liquid scintillation counting is based on the conversion of the energy of a particle emitted by a radioactive nucleus to light energy by means of a scintillating chemical. The scintillations are detected by a photomultiplier (PM) tube. The electrical signals from the PM tube are amplified and sent through a simple multichannel analyzer (three or four channels at most) where sorting into energy takes place. The counts in

each channel are displayed on a scaler and may be read out on paper tape, punched tape, or magnetic tape.

Liquid scintillation counting is used primarily for the counting of beta emitters although it can also be used for alpha-emitting isotopes.

When liquid scintillation counting is used to determine a radionuclide in aqueous solution, the water sample is dissolved or dispersed in a larger volume of organic solvent containing the scintillating chemical. A widely used mixture for aqueous solutions was dioxane-naphthalene containing the scintillator 2,5-diphenyloxazole (PPO) and a secondary scintillator used to shift the wavelength of the scintillations to the most sensitive spectral region of the PM tube. Much of the tritium data reported in the literature was determined by use of the above scintillation mixture. The dioxane-PPO combination has been superseded by proprietary scintillators that produce gels when mixed with water in proper ratios. The newer scintillators have approximately doubled the sensitivity of liquid scintillation counting for tritium. Since the composition of the proprietary mixtures is not available, these are listed by trade name in the "Reagent" section.

While the mechanism of liquid scintillation counting is not completely understood, it seems clear that the energy transfer is a two-stage process, with initial energy transfer to the solvent followed by transfer from the solvent to the scintillator. Many substances, including water, interfere in the energy-transfer process to quench the scintillations and reduce the count rate. Excessive salt content, certain metals, and organic compounds quench in varying degree. Colored substances may quench by light absorption in addition to interfering with energy transfer. Quenching substances are generally removed by vacuum distillation.

The quenching effect of water is compensated by using a constant volume of water and constant ratio of water sample to scintillator mixture in both samples and standards. The count rate of a particular sample depends on both the volume of sample and

the ratio of liquid scintillator mixture to water sample. As the fraction of water sample in the water-scintillator mixture increases, count rates increase until a point is reached where the quenching effect of the additional tritiated water exceeds the effect of the increased radioactivity. It is found that a practical compromise between maximum sample volume and scintillator volume provides optimum sensitivity. The maximum on the curve of activity versus volume of tritiated water (in a constant overall volume) is a rounded plateau. Therefore, the proportion of water sample to scintillating liquid mixture is not critical and is easily reproducible in routine work.

The permissible ratio of water sample to liquid scintillator mix is also controlled by physical stability of the gel formed.

A detailed description of the method is given by Schroder (1971).

3. Interferences

There are no interferences in the analytical method when electrolysis is included. Distillation is used to remove both quenching substances and radionuclides that could contribute to excess counts. Distillation and electrolysis are fully effective in removing inorganic salts, high-boiling organic compounds, and gaseous radioisotopes. Krypton and all other gases are stripped out in the electrolysis owing to prolonged bubbling of oxygen and hydrogen through the sample.

Further protection against interferences is provided by the energy discrimination in the liquid-scintillator analyzer and the external standard-ratio test.

4. Apparatus

4.1 *Autopipet*, 25-ml maximum capacity.

4.2 *Counting equipment*. Liquid scintillation spectrometer; counting systems capable of meeting the following specifications:

Background—not to exceed 5 cpm at sea level in tritium channel.

Counting efficiency—not less than 24 percent with optimum sample-scintillator mixture and polyethylene vials.

Sample capacity—at least 100 samples.
 Operation—programmable and automatic.
 Internal check—an external standard and ratio computation capability required.
 Readout—automatic printout.

4.3 *Electrolysis unit.* Contains the following components:

4.3.1 Electrolysis cells. See figure 8. The Östlund cell has a mild-steel cathode (where reduction of hydrogen isotopes occurs) and stainless-steel anode. The glass envelope is designed to attach directly to a vacuum-distillation apparatus.

4.3.2 Power supply, direct current, at least 6 amperes at 30 volts.

4.3.3 Freezer, floor-model, large enough to hold two rows of five electrolysis cells.

4.3.4 Exhaust lines, to vent the explosive mixture of oxygen and hydrogen generated in electrolysis.

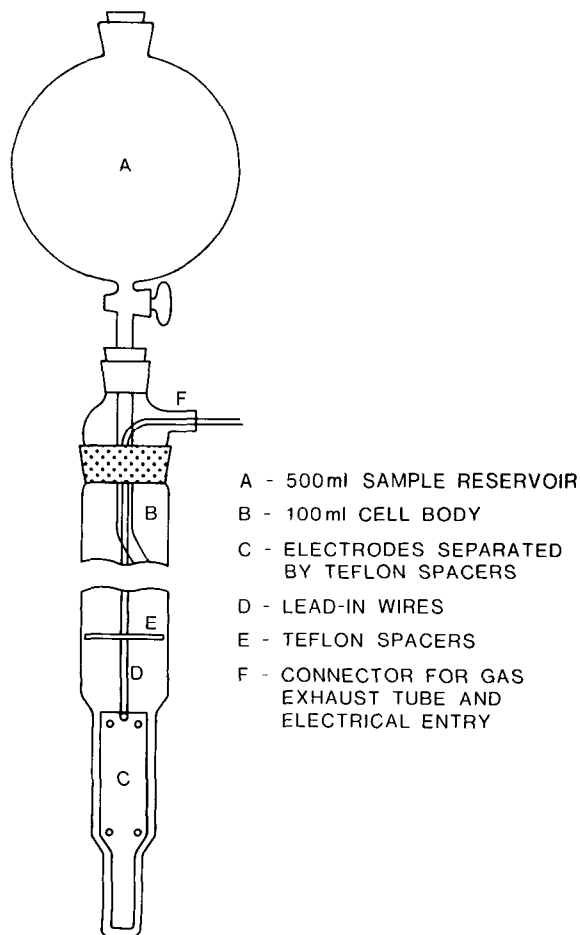


Figure 8.—Östlund electrolysis cell.

4.4 *Pipets, 8-ml.*

4.5 *Vacuum-distillation apparatus.* Consists of a 100-ml round-bottom flask as the distillation flask and a 125-ml round-bottom flask as the condenser flask. The distillation flask is heated with a rheostat-controlled mantle and the condenser flask dips into a Dewar containing isopropanol-dry ice. The two flasks are connected by a 20-mm diameter U-tube, 10-cm long with ground-glass connectors and stopcock for application of vacuum. Heating tape is coiled around the U-tube connecting the two flasks.

5. Reagents

5.1 *Scintillator, Instagel* (Packard Instrument Co.) for low-temperature counting (1° – 4° C). A preblended gel-forming scintillator designated 3A70* (Research Products International) for room-temperature counting.

5.2 *Sodium peroxide*, reagent-grade.

5.3 *Tritium standard solution:* Appropriate standards are prepared by the dilution of NBS standard tritiated water with "dead" water, that is, water containing less than 1 Tu.

5.4 *Water, "dead":* The tritium blank introduced by reagents and leakage during electrolysis must be tested at intervals by analyzing "dead" water (water with no measurable tritium content), in exactly the same procedure as for a normal water sample. It is very difficult to confirm that a water is truly "dead," and it is usually necessary to make the assumption that water from a deep well in a confined aquifer a hundred kilometers or more from the recharge area is "dead." This assumption can be correct only if the well is pumped sufficiently to expel all meteoric water that may have entered the well and surrounding aquifer by leakage.

6. Procedure

6.1 Electrolysis. (In electrolysis and all other steps, heat-dried glassware is used.)

6.1.1 Distill 55-ml volume of water sample in the vacuum-distillation apparatus. The unit is evacuated before use, and the water

sample is protected from atmospheric moisture during distillation. Distill to dryness. Recovery is usually slightly less than the original volume because of water of hydration remaining in the salts residue and droplets on the walls of the apparatus. The tritium fractionation attributable to nondistilled water is insignificant.

6.1.2 Transfer the distillate to a clean and dry Östlund electrolysis cell (fig. 8), add 0.75 g of sodium peroxide, add 50 ml of the distilled-water sample, and stopper the cell. An argon atmosphere is maintained in the reservoir to eliminate contact with atmospheric moisture.

6.1.3 Prepare a blank sample ("dead" water) for electrolysis using the above procedure. Prepare a standard for electrolysis (200 Tu is a convenient concentration range) using the above procedure.

6.1.4 Set up one blank, one standard, and four samples in series in the electrolysis bath. A larger number of samples may be used if sufficient voltage is available from the electrolysis power supply. The tritium enrichment for one group of samples is determined by the enrichment of the standard in series with the group.

6.1.5 Proceed with the electrolysis after samples have been cooled in the cold chest. The temperature of the ethylene glycol-water coolant bath is maintained at 0°C throughout the process. Electrolysis from 50 ml to approximately 10 ml using 4-ampere current.

6.1.6 Neutralize the highly caustic solution in the cells to permit full recovery of tritium and to avoid mechanical and corrosion problems in subsequent steps. Disconnect a cell from the electrolysis line, and while protecting from the atmosphere insert a disposable pipet through the hole in the Teflon spacer. Bubble carbon dioxide through slowly. About 5 min and 1 liter of carbon dioxide are required to complete neutralization. A precipitate of sodium carbonate forms.

6.1.7 Distill the neutralized sample into a small tared Pyrex bulb using vacuum-distillation apparatus. The sample is cooled (but not frozen) in liquid nitrogen. Attach the still-liquid sample to the inlet of the distilla-

tion apparatus and apply vacuum. The sample first bubbles to release trapped gases and then freezes. Apply a heat lamp or heat gun to distill the sample into the liquid-nitrogen-cooled receiving bulb. Weigh the bulb after completion of distillation to determine the volume of the water sample collected.

6.2 Counting.

6.2.1 Pipet 8.00 ml of the distillate from the preceding step into a 25-ml polyethylene vial, and add 14 ml of scintillator mix. The choice of scintillator depends on the type of liquid scintillation spectrometer to be used for counting. Instagel is used with the instruments that operate at cold temperature (3°C) and 3A70* is used with the instruments that operate at room temperature. Cap the vial and mix. Heat the Instagel-sample mixture on a hotplate at approximately 100°C for 2 or 3 min. This clarifies the mixture. The 3A70*-sample mixture does not require heating. The above operation is carried out under subdued red light to filter out the blue region of the spectrum. This minimizes excitation of fluorescence background in the sample.

6.2.2 Prepare three blanks and two standards in the same manner as the samples. Place one standard in the 2d counting position in the spectrometer and one in the 10th position. Place blanks at intervals throughout the run of 10-14 samples.

6.2.3 Place three sealed standards (triated toluene in glass-sealed scintillator solution) in the group. One standard goes in the first counting position to permit monitoring the instrument before counting the samples. The remaining sealed standards are placed near the blanks.

6.2.4 Allow prepared samples to remain in the dark in the liquid scintillation spectrometer for several hours before counting begins. This allows decay of fluorescence and chemiluminescence. A minimum of 8-hr standing is required with Instagel and 12 hours with 3A70*.

6.2.5 Count each vial five times for 100 min. Total counting time for one sample is 500 min.

6.2.7 Program the instrument to perform the external-standard ratio analysis on samples, standards, and blanks at the end of the counting run (see instrument instruction manual). This procedure is a check for quenching. The ratio of low-energy counts in channel A of the spectrometer is established for both tritium and an external standard placed near the sample vial. The value of R in the following equation should be constant to within ± 0.2 .

$$R = \left[\frac{\text{Counts in A tritium}}{\text{Counts in B}} \right] \left[\frac{\text{Counts in B standard}}{\text{Counts in A}} \right].$$

Individual samples that fall outside this range must be reanalyzed. If all values of R fall outside this range, the scintillator has deteriorated and must be replaced.

7. Calculations

Several statistical schemes have been presented for the calculation and verification of tritium data, each intended to optimize a particular analytical situation. In the present analytical procedure the repeated counting of individual samples has the effect of averaging out short-term fluctuations. Statistical checks have shown that highest precision, in this analytical situation, is attained by the use of longer term average values for the samples and standards.

Counting efficiency and background values are determined with tritium standards whenever a new lot of scintillator is used. Counting-efficiency data and background data from standards and blanks run with each set are also determined. The new data from each set are averaged into the data from the preceding sets, thus creating a moving average value for counting efficiency and background. As new efficiency and background data appear they displace older data entered into the moving average. Data from four or five valid runs (no quenching or other aberration) enter into the moving average used at any given time.

7.1 Tritium efficiency factor (E). Use equation 2:

$$E = \frac{\bar{c}_n}{d_n (e^{-\lambda t_n})}, \quad (2)$$

where

\bar{c}_n = average count rate of standard (cpm) corrected for background and blank,

d_n = disintegration rate of standard (dpm), corrected for blank ($\bar{S} - \bar{B}$),

λ = decay constant of tritium (4.685×10^{-3} month $^{-1}$),

t_n = elapsed time between certification of the standard and time of count in same units as λ ,

where

\bar{S} = moving average count rate (cpm) of the standards, and

\bar{B} = moving average count rate (cpm) of the blanks.

7.2 Calculation of tritium concentration: Use equation 1. The chemical recovery factor (f) is an enrichment factor when electrolytic enrichment is applied to the sample.

$$\text{pCi tritium/l} = \frac{1,000\bar{c}}{KVEf(e^{-\lambda t})}, \quad (1)$$

where f is electrolytic enrichment factor determined by standard included in the run,

$$f = \frac{\text{cpm/ml after electrolysis}}{\text{cpm/ml before electrolysis}}.$$

7.3 Conversion of tritium concentration in pCi/l to tritium units.

$$\text{Tritium concentration in Tu} = \frac{\text{pCi tritium/l}}{3.22}.$$

8. Report

Concentrations in both tritium units and picocuries per liter are reported to two significant figures down to the minimum detection level (MDL). The latter can only be estimated because of the very pronounced effect of altitude on the background count. At 5,000 ft (1,500 m) it is estimated at 25 Tu for the liquid scintillation counting of an electrolytically enriched sample.

9. Precision

Precision is dependent on altitude in the same way as MDL. At 500 Tu reproducibility

is approximately ± 20 percent. Precision improves with increasing concentration and is improved by electrolytic concentration of samples with lower tritium concentration.

Reproducibility for samples enriched by electrolysis is limited by the reproducibility of electrolysis (approximately ± 3 percent).

References

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Tritium

Electrolytic enrichment—liquid scintillation method, Reston lab (R-1174-76)

Parameters and codes: Tritium, dissolved (pCi/l): 07005
Tritium, in water molecules (Tu): 07012

1. Application

The limit of detection of tritium by the liquid scintillation counting method (R-1173-76) is about 60 Tu (190 pCi/l). Many surface-water and most ground-water samples contain less than 60 Tu, and cannot be analyzed directly. Concentration of the tritium in low-tritium samples by electrolysis before counting by liquid scintillation permits the analysis of waters containing as little as 1 Tu (3 pCi/l).

2. Summary of method

When water is decomposed to H₂ and O₂ gas by electrolysis there is a strong isotope fractionation effect which results in the heavier isotopes (tritium in particular) being concentrated in the remaining liquid phase. Under the proper conditions, recovery of more than 70 percent of the initial tritium is possible. Thus, if a sample is reduced from 500 ml to 5 ml by electrolysis, the tritium in the residual 5 ml will have been concentrated

by at least: $\frac{500 \times 0.7}{5} = 70$ times. When such

an electrolyzed sample is counted using the procedure described in method R-1173-76, tritium levels as low as 1 Tu can be detected.

The electrolysis procedure used is essentially that described by Östlund and Werner (1962). The sample, after distillation, is made basic with NaOH or Na₂O₂ and electrolyzed in glass cells (Östlund cells) with

nickel and soft iron electrodes. (See fig. 8, method R-1172-76, for diagram of electrolysis cell.) During operation, the cells are kept at 0°–1°C to improve electrolytic tritium recovery and to minimize loss of sample by evaporation. A maximum of 100 ml is electrolyzed in the cell. If larger samples are to be electrolyzed, the sample is periodically added to the cell from the reservoir as electrolysis proceeds.

Electrolysis proceeds at 6 amperes until less than 25 ml remains. Then the current is reduced in steps to as low as one-half ampere as the remaining volume decreases to the desired 5-ml final volume. Electrolysis from a starting volume of 100 ml requires about 4 d.

Following electrolysis, the sample water is separated from the electrolyte by vacuum distillation and is then ready to be counted.

Electrolysis is performed in sets of cells connected in series to a constant voltage, current-limiting power supply. Each set includes an electrolysis standard, a blank, and from 4 to 10 samples.

3. Interferences

Samples are distilled before and after electrolysis, and are thoroughly gas-stripped by the H₂ and O₂ produced during the electrolysis itself. Thus all potential interfering substances are effectively removed, and no radioactive or other interferences remain in the sample ready for counting.

The major interference with low-level tritium analysis is contamination by tritium it-

self. The electrolyte may contain tritium, or the sample may pick up tritium during excessive exposure to the laboratory atmosphere. To minimize contamination, it is important that sources of tritium above levels naturally present in the air be rigorously excluded from the laboratory. These sources include luminous watches and such high-tritium samples as may result from tracer tests.

Samples of "dead" water should be run through the entire electrolysis and counting process as blanks to monitor contamination and to permit corrections to be made to the final reported tritium content (see section below).

4. Apparatus

The apparatus required is the same as that described in method R-1173-76 with the addition of the following:

Östlund electrolysis cells. (See fig. 8, method R-1172-76.)

Vacuum-distillation apparatus, (1) for predistillation, capable of handling volumes up to 500 ml, and (2) for distillation after electrolysis, capable of handling from 3 to 10 ml.

Freezer for cooling electrolysis cells.

5. Reagents

As specified in method R-1173-76 with the addition of the following:

Electrolyte, NaOH or Na₂O₂.

Electrolysis standard, a tritium standard solution prepared as described in method R-1173-76, sec. 5.2, and containing about 1 dpm/ml.

6. Procedure

Perform electrolytic enrichment as described in sec. 2 above, then follow procedure described in method R-1173-76.

7. Calculations

7.1 Enrichment factor. The enrichment factor, f , required to calculate the sample tritium content from the count data (see

method R-1173-76) is calculated using equation 1:

$$f = \frac{V_0}{V_f} \times \frac{V_0^{-(1/\beta)}}{V_f}, \quad (1)$$

where

V_0 = volume of sample before electrolysis,

V_f = volume of sample following electrolysis, and

β = the separation factor.

The electrolysis standard with each set is counted as if it were a sample and its tritium content determined. Then:

$$f_{std} = \frac{Tu_f}{Tu_0}$$

where

Tu_f = Tritium content of electrolysis standard after electrolysis,

Tu_0 = Tritium content of electrolysis standard before electrolysis, and

f_{std} = standard enrichment factor.

The standard enrichment factor is then substituted for "f" in equation 1 and β is calculated for the set.

7.2 Calculation of tritium concentration. Calculate tritium concentration in the sample in the manner described in method R-1173-76.

8. Report

Report as described in method R-1173-76.

9. Precision

There are uncertainties in each of the terms in equation 1 leading to f . These are the weighing errors in V_0 and V_f , and variations in the electrolysis process itself giving rise to variations in β . Experience suggests that the one standard deviation error of f (σ_f/f in equation 5, method R-1173-76) is about 5 percent.

There is also error associated with the value of the blank which is used to correct for sample contamination by reagents and exposure in the laboratory. Under favorable conditions, the error in the blank may be as

small as ± 0.02 Tu (Östlund and others, 1974). In routine work, the error in the blank is taken as equal to the value of the blank correction itself—usually from 0.1 to 0.3 Tu. Thus, although it is sometimes possible to count a sample to a precision of less than 0.1 Tu, the real precision of routine tritium analyses is limited by the blank error to ± 0.1 to ± 0.3 Tu.

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Uranium, dissolved Fluorometric method—direct (R-1180-76)

Parameters and codes: Uranium, dissolved ($\mu\text{g/l}$): 22703
Uranium, dissolved (pCi/l): 80010

1. Application

The method is suitable for the determination of uranium in nonsaline waters ($<10,000$ mg/l dissolved solids) in which uranium fluorescence is quenched less than 30 percent. If quenching exceeds 30 percent, it is advisable to use the extraction method. The latter method is much more time consuming. Therefore, it is usual practice to apply the direct fluorimetric method as a first step unless previous analysis of samples from a particular area has shown that the simple approach is not possible.

The minimum detection limit varies with the properties of the sample, flux, and fluorimeter, but is normally $0.3 \mu\text{g/l}$.

2. Summary of method

The fluorimetric method of determining uranium is among the most sensitive and specific of analytical methods. The intense fluorescence of uranium when fused in a sodium fluoride-sodium carbonate-potassium carbonate flux is utilized to determine quantitatively the amount of uranium present in the sample. In its simplest form the analysis is carried out by fusing a dry residue of the evaporated-water sample in fluoride-carbonate flux, allowing this to solidify into a small disk, and determining the fluorescence under ultraviolet light in a reflection-type fluorimeter. Chromium, copper, manganese, and a few other elements in water quench the fluorescence in varying degree. When the quenching elements are in relatively low con-

centration, quench-compensation techniques may be used. When quenching elements are present in relatively high concentration, it is necessary to purify the uranium by extraction. This technique is described as "Fluorometric method—extraction procedure" (R-1181-76).

Although the fluorescence of the sample is directly proportional to the uranium concentration (disregarding quenching effects), it is not possible to use a constant calibration straight-line plot of fluorescence against concentration. This is a result of variation in properties between batches of flux, variations in the fluxing temperature, possible surface oxidation during fluxing, and variations of uranium impurity in different batches of flux. The above effects are minimized by running uranium standards with each set of samples so that a new calibration of concentration against fluorescence is made under the conditions existing for each set of analyses.

The materials used for the preparation of the flux always contain a small amount of uranium. Fluorescence from this source plus reflected light not absorbed by the filters in the fluorimeters make up the blank. The fluorescence component of the blank is subject to quenching while the reflectance component is not. The blank for a highly quenched sample is, therefore, less than the blank for a sample with relatively low quenching. A graphical method of compensating for this effect on the blank value was developed by Thatcher and Barker (1957).

The following method is similar to that described in Water-Supply Paper 1696-C (Barker and others, 1965) for the determination of uranium in nonsaline water.

3. Interferences

Direct spectral interference is not a problem in the fluorimetric method. Cadmium fluoresces in high carbonate flux disks at approximately the same wavelength as uranium (Booman and Rein, 1962, p. 102), but interference from this source is unlikely in most natural waters. High concentrations of salt cause difficulty in the preparation of the flux disks. The quenching effect of transition metals has been cited above.

4. Apparatus

4.1 *Crucible tongs*, platinum tipped for holding hot platinum dishes.

4.2 *Fluorimeter*. A reflection-type instrument of high sensitivity equipped with a sample carriage to accept small disk-shaped solid samples is required. The sample cavity should be approximately 35 mm in diameter and 5-mm deep. Instructions herein pertain to the Jarrell-Ash Model 26-000 instrument, but any fluorimeter that fulfills the above requirements may be used.

4.3 *Fusion apparatus*. The rotary fusion machine developed by Stevens and others (1959) and modified by Barker and others (1965) is used (fig. 9). A rotating sample carriage is mounted above a ring of burners and is slowly revolved during the fusion to assure that each sample receives the same heating. The samples are contained in platinum fusion dishes resting on quartz rods. The fusion unit is tilted approximately 30° during part of the fusion so that molten flux washes the sides of the fusion dishes to sweep down any sample residue that may adhere. The design of the burner must be adapted to local gas composition and pressure to obtain the optimum temperature.

4.4 *Fusion dishes*. The dishes are fabricated of platinum to a shallow-dish shape that provides maximum exposure of sample disk surface (for high fluorescence sensitivity) compatible with adequate thickness for strength (fig. 10). The rounding of the bottom permits easy removal of the solidified

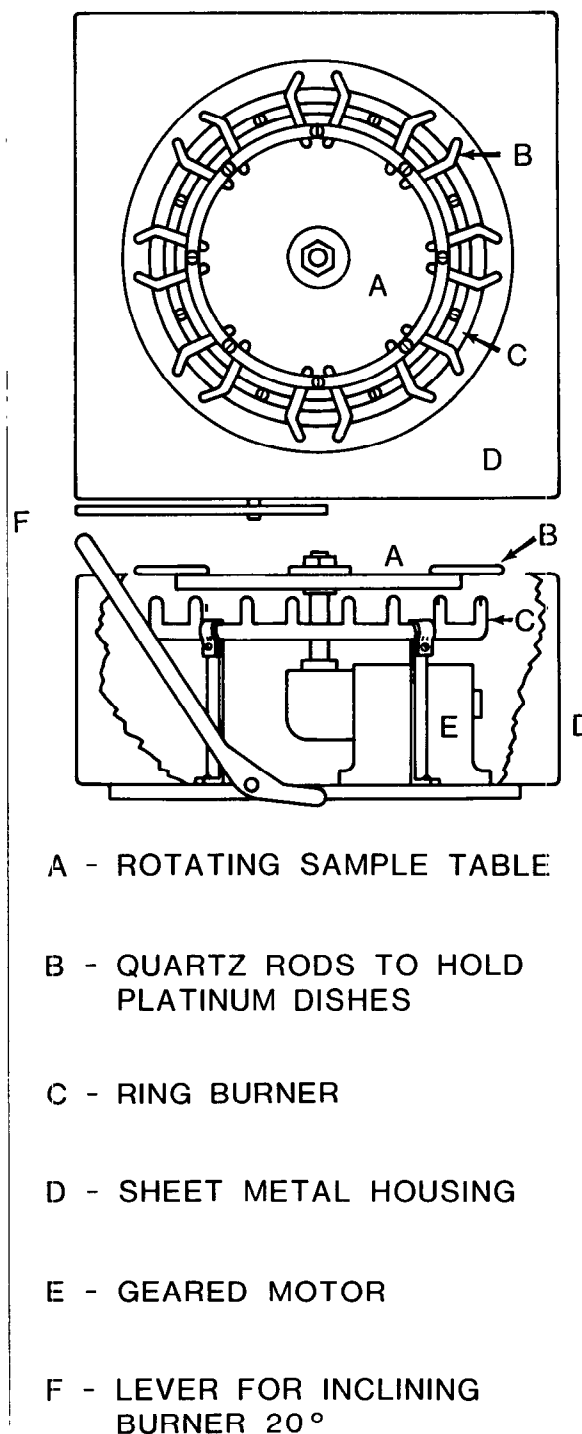
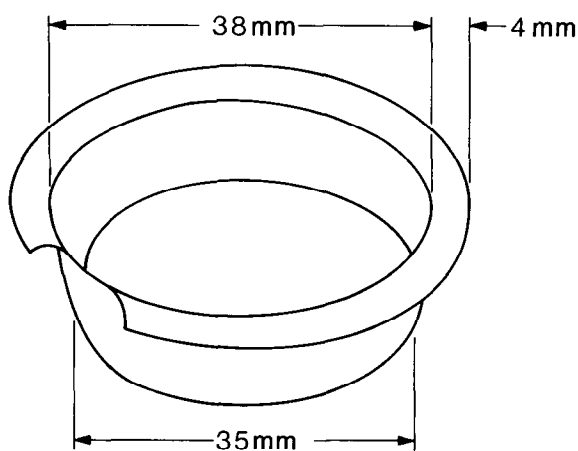


Figure 9.—Stevens apparatus for fusion and mixing of sample and flux in uranium determination.

ty) compatible with adequate thickness for strength (fig. 10). The rounding of the bottom permits easy removal of the solidified



DEPTH AT RIM - 10mm
DEPTH AT CENTER - 12mm

Figure 10.—Platinum dish for use in Stevens apparatus.

flux disk. An identifying number is stamped into the lip of each dish.

4.5 *Infrared drying lamps*: Dual 250-watt infrared drying lamps in a protective metal shield are mounted on a ringstand for variable heat adjustment.

4.6 *Micropipet*, 50- μ l capacity, Eppendorf type, for addition of uranium standard.

4.7 *Mill*. A 5- to 6-liter Pyrex glass-jar mill containing 15 cm by 2.5 cm cylindrical Lucite rods is used to mix the flux.

4.8 *Pipets*, volumetric 1-, 2-, 3-, 4-, 5-, 6- and 10-ml.

4.9 *Polyethylene jars*, wide-mouth, 4-liter screw-capped, for storing flux.

5. Reagents

5.1 *Chromium solution*, 1 ml = 30 μ g Cr: Dissolve 0.085 g of $K_2Cr_2O_7$ in distilled water and dilute to 1,000 ml. Weight and volume measurements need not be exact.

5.2 *Copper solution*, 1 ml = 60 μ g Cu: Dissolve 0.236 g of $CuSO_4 \cdot 5H_2O$ in distilled water and dilute to 1,000 ml. Weight and volume measurements need not be exact.

5.3 *Manganese solution*, 1 ml = 20 μ g Mn: Dissolve 0.081 g of $MnSO_4 \cdot 5H_2O$ in distilled water and dilute to 1,000 ml. Weight and volume measurements need not be exact.

5.4 *Sodium fluoride solution*, 1 ml = 0.01 g NaF: Dissolve 10 g of dry sodium fluoride in distilled water and dilute to 1,000 ml.

5.5 *Uranium standard solution I*, 1 ml = 100 μ g U: Dissolve 0.1773 g of reagent-grade uranyl acetate dihydrate in approximately 500 ml of distilled water. Add 10 ml of concentrated nitric acid and dilute to 1,000 ml in a volumetric flask. Store in a Teflon bottle.

5.6 *Uranium standard solution II*, 1 ml = 1.00 μ g U: Dilute 10.0 ml of uranium standard solution I to 1,000 ml with distilled water. Store in a Teflon bottle.

5.7 *Flux*: Using anhydrous powdered reagent-grade chemicals, weigh out 910 g of Na_2CO_3 , 910 g of K_2CO_3 , and 180 g of NaF, and rough-mix in the glass-jar mill using a large porcelain spatula, or Lucite rod. Add the small Lucite rods, stopper tightly with a polyethylene stopper, place the jar on the mechanical rollers, and dry-mix overnight.

6. Procedure

6.1 *Determination of flux constants*: It is necessary to determine r (the fraction of reflected light in the blank) and f (the fraction of fluorescent light in the blank) for each batch of flux. These "flux constants" are used for all analyses made with the given batch of flux. Two calibration curves are prepared as shown in figure 11. The calibration curve X is prepared with pure uranium solutions and the calibration curve Y is prepared with uranium solutions containing a constant amount of quenching agent. The two curves intersect (P) at a negative uranium concentration. The intersection of the curve X with the fluorescence axis is point A, the unquenched blank. The intersection P of X and Y is point B, the reflected light. The fraction of reflected light r is B/A and the fraction of fluorescent light f in the blank reading is $1-r$.

The procedure is as follows:

6.1.1 Measure 1 ml of sodium fluoride solution and the following volumes of uranium standard solution II (microburet) into platinum fusion dishes.

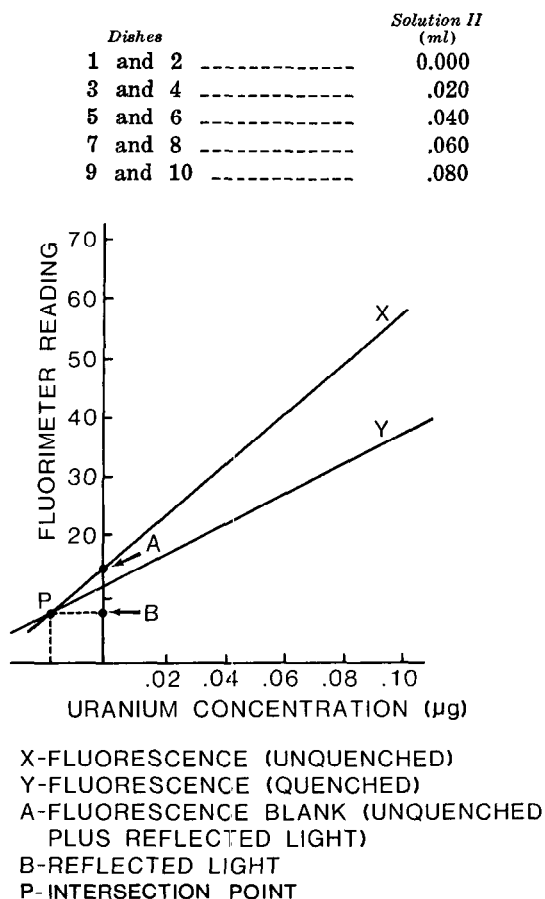


Figure 11.—Uranium calibration curve.

6.1.2 To the even-numbered dishes, add 1 ml of chromium solution.

6.1.3 Evaporate the solutions to dryness under the infrared lamps. Do not permit the samples to bake as this can result in loss of uranium, although the sodium fluoride added as the first step minimizes loss by overheating.

6.1.4 Fusion procedure: To each of the dishes add 2 g of the flux mixture. Spread and bank the flux with a glass rod so that any solids on the vertical walls of the dishes will be covered.

6.1.5 Place the dishes on the rotating table of the Stevens fusion apparatus, and incline it by operating the positioning lever. Ignite the burner ring, adjust to maximum heat, and heat the dishes until the flux is completely melted. This requires about 5 min. Allow the fusion table to rotate in the inclined position for an additional 2 min. Re-

turn the table to the level position, and continue heating the melt for an additional 3 min at the same temperature.

6.1.6 Turn the heat control to the intermediate setting and heat at this temperature for 3 min.

6.1.7 Turn to the low setting and heat for 3 min. Turn off the burner and allow the dishes to cool for 8 min with the fusion table still rotating. Finally, place the dishes in a desiccator, and cool for at least 30 min before measuring fluorescence.

6.1.8 Measurement of fluorescence: The following instructions apply to the Jarrel-Ash fluorimeter. Modify if other fluorimeters are used. Allow the instrument to warm up 30 min before use.

6.1.9 Set the fluorimeter reading to zero using the zero-adjustment knob. Push the empty sample tray all the way in, depress the X.01 key, and adjust to zero using the screw adjustment. Remove the blank flux disk from the platinum dish by inverting it on a clean piece of paper. Place the disk in the fluorimeter tray and push into measurement position. Depress the X.1 key and adjust the sensitivity so that a reading of 10 (on a scale of 100) is obtained for the blank.

6.1.10 Remove the blank disk and recheck the zero setting. Use a soft-bristle brush to remove any particles sloughed into the sample tray from the preceding disk. If the zero needs readjustment, repeat step 6.1.9 until the empty holder reading is zero when the blank reading is 10. The "fluorescence" reading of the empty holder is minimized by painting with a colloidal graphite mixture such as Aqua-dag. This must dry before use. Repainting is required at intervals.

6.1.11 Read the fluorescence of the standard and sample disks using the X.1 scale, if possible, or X1 and X10 scales if needed.

6.1.12 Plot the fluorescence of the disks as a function of the weight of uranium (fig. 11). Draw the best straight lines X and Y through the sets of points for the quenched and unquenched disks. Determine B, A, and r and f as above.

6.1.13 Repeat the calibration substituting 1 ml of manganese solution for the chromium solution.

6.1.14 Repeat the calibration substituting 1 ml of copper solution for the chromium solution.

6.1.15 Average the values of r and f determined for the three quenching elements as above. These mean values of r and f are used for all analyses using this batch of flux.

6.2 Analysis of the water sample.

6.2.1 Four samples may be analyzed simultaneously using the Stevens fusion apparatus with 20 positions for samples, when analyses are run in duplicate. One milliliter of sodium fluoride solution is added to the 20 platinum dishes. Two dishes serve as blanks. Standard uranium ($0.06 \mu\text{g}$) is added to each of two dishes. Four 7-ml aliquots of each sample are pipetted into four dishes. Standard uranium ($0.06 \mu\text{g}$) is added to two of them.

6.2.2 Proceed with the analysis as in steps 6.1.3 through 6.1.11 above.

7. Calculations

7.1 Determine the quenching factor, Q , for each sample from the equation:

$$Q = \frac{D - A}{C - B} = \frac{\Delta I_s}{\Delta I_n},$$

where

Q = ratio of uranium fluorescence under quenching conditions to the fluorescence under no quench, for a given sample,

A = mean fluorimeter reading of unspiked samples,

B = mean fluorimeter reading of blank disks,

C = mean fluorimeter reading of standard disks,

D = mean fluorimeter reading of sample disks containing uranium spike,

ΔI_s = fluorescence increment of spiked sample, and

ΔI_n = fluorescence of the standard.

Note that the equation applies only when the amount of uranium spike in the sample is equal to uranium in the standard.

7.2 Calculation of the corrected blank value for each sample: The blank value to be used with an individual water sample must be somewhat less than the blank measured instrumentally on the pure sodium fluoride-sodium carbonate disk because of quenching in the water sample of that portion of the blank value contributed by uranium impurity in the flux. Since a blank that represents conditions in the sample cannot be prepared, it is necessary to calculate the blank value for each sample on the basis of the blank measured for the disk of pure fluoride-carbonate flux. The contribution of reflected light to the blank is assumed to be the same for the sample disks and the pure flux disk. The calculation is simply:

$$B_s = (QfB_f) + (rB_f),$$

where

B_s = sample blank.

B_f = blank obtained with disk of pure flux,

f = fraction of fluorescent light for the batch of flux used,

r = fraction of reflected light for the batch of flux used, and

Q is defined in section 7.1.

7.3 Concentration of uranium in the sample: This is calculated using equation:

$$\text{g/l of U} = \frac{S}{\Delta I_n} \left[\frac{A - B_s}{Q} \right] \left[\frac{1,000}{V} \right],$$

where

S = micrograms of uranium in the standard, and

V = sample volume in ml and the other terms are as defined in sections 7.1 and 7.2.

If it is known from previous experience with water from a particular source that the quenching factor Q is always greater than 0.7 (quenching less than 30 percent), it becomes possible to omit the determination of Q and combine equations under 7.1 and 7.3 to obtain the following simplified expression:

$$\mu\text{g/l of U} = \frac{S(A - B_s)}{\Delta I_s} \left[\frac{1,000}{V} \right].$$

8. Report

Report concentrations less than 1.0 $\mu\text{g}/\text{l}$ to one significant figure. Above 1.0 $\mu\text{g}/\text{l}$, report two significant figures. Occasionally the radioactivity is reported in pCi/l. The conversion factor is 1 $\mu\text{g}=0.33$ pCi when only the radioactivity of uranium-238 is considered. Natural uranium contains 0.72 percent of uranium-235, and normally uranium-238 is considered to be in equilibrium with an equal activity of uranium-234. The conversion factor is 1 $\mu\text{g}=0.68$ pCi when all three isotopes are included.

9. Precision

Precision is approximately \pm MDL or ± 15 percent, whichever is larger. The MDL is a function of quenching, fluorescence intensity of the flux, and uranium impurity in the flux. It may be as low as 0.1 $\mu\text{g}/\text{l}$ with a sample having no significant quenching an-

alyzed with a relatively pure flux, and as high as 0.5 $\mu\text{g}/\text{l}$ when a highly quenched sample is analyzed with a flux having relatively high uranium impurity. Under average conditions the MDL is 0.3 $\mu\text{g}/\text{l}$.

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Uranium, dissolved

Fluorometric method—extraction procedure (R-1181-76)

Parameters and codes: Uranium, dissolved ($\mu\text{g/l}$): 80020
Uranium, dissolved (pCi/l): 80015

1. Application

The method is applied to water samples where the reduction of uranium fluorescence by quenching exceeds 30 percent (as determined in "Fluorometric method—direct" (R-1180-76)), the concentration of total dissolved solids exceeds approximately 10,000 mg/l, or a minimum detection level lower than 0.3 $\mu\text{g/l}$ is desired.

2. Summary of method

Uranium is separated from quenching elements and excessive salt concentrations in a two-step separation procedure developed by Smith and Grimaldi (1954). Uranium is coprecipitated, as uranyl phosphate, on aluminum phosphate from a large-volume water sample. Several quenching elements are carried down by the precipitate. Final purification is made by dissolving the phosphate precipitate in dilute nitric acid and extracting with ethyl acetate or ethyl ether in the presence of a salting agent. The organic solution is evaporated to dryness in a platinum dish, and the fluorescence is determined after fusion of the dry residue in sodium fluoride-sodium carbonate flux.

Barker and others (1965) modified the procedure slightly and evaluated the application to natural waters. The present procedure uses magnesium nitrate (Hellman and Wolf, 1952) to "salt-out" uranium from the nitric acid solution of the precipitate into the ethyl ether phase. The magnesium salt is slightly more effective than the aluminum salt and usually contains less uranium impurity, thus giving a lower blank correction.

3. Interferences

All interferences in natural waters are removed by the separation steps and have no effect. The method has not, however, been extensively tested with industrial wastes, mine waters, and other waters that may have unusually high concentrations of heavy metals. When such waters are encountered it is advisable to run a spiked sample containing a known increment of uranium through the analytical procedure to test for possible residual quenching. A quenching correction can then be made as in "Fluorometric method—direct" (R-1180-76) based on the percentage of reduction of the expected fluorescence from the known increment of uranium.

4. Apparatus

- 4.1 *Centrifuge.*
- 4.2 *Centrifuge tubes, 40- or 50-ml capacity Pyrex tubes with polyethylene screw-type caps.*
- 4.3 *Evaporating dishes, Teflon, 125 ml.*
- 4.4 *Fluorimeter: See method R-1180-76.*
- 4.5 *Fusion apparatus: See method R-1180-76.*
- 4.6 *Fusion dishes: See method R-1180-76.*
- 4.7 *Micropipet, 50- μl -dispensing pipet, Eppendorf type.*
- 4.8 *Pipet and control, 5 ml.*
- 4.9 *Polyethylene jars: See method R-1180-76.*
- 4.10 *Ultrasonic generator, 500-watt model.*

5. Reagents

5.1 *Aluminum nitrate solution, 0.2 M:* Dissolve 15 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in distilled water and dilute to 200 ml.

5.2 *Ammonium hydroxide, concentrated.*

5.3 *Ammonium nitrate solution, 1 ml = 10 mg NH_4NO_3 :* Dissolve 10 g of reagent-grade ammonium nitrate in distilled water and dilute to 1,000 ml.

5.4 *Diammonium hydrogen phosphate solution, 0.090 M:* Dissolve 12 g of $(\text{NH}_4)_2\text{HPO}_4$ in distilled water and dilute to 1,000 ml.

5.5 *Ethyl ether.*

5.6 *Magnesium nitrate reagent, 5.0 N in $\text{Mg}(\text{NO}_3)_2$, 0.5 N in HNO_3 :* Dissolve 640 g of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in the minimum volume of hot distilled water in a 1-litre beaker. Pour into a 1,000-ml volumetric flask, add 32 ml of concentrated HNO_3 , dilute to volume, cool to room temperature, and again dilute to volume.

5.7 *Methyl red indicator solution:* Dissolve 0.1 g of methyl red (dimethylaminoazobenzenecarboxylic acid) in 250 ml of 60 percent ethanol.

5.8 *Nitric acid, concentrated.*

5.9 *Uranium standard solution I, 1 ml = 100 μg U:* See method R-1180-76.

5.10 *Uranium standard solution II, 1 ml = 1.0 μg U:* See method R-1180-76.

5.11 *Uranium standard solution III, 1 ml = 0.01 μg U:* Pipet 10 ml of uranium standard solution II and 5 ml of concentrated HNO_3 into a 1,000 ml volumetric flask, and dilute to volume with distilled water. Mix thoroughly, and store in a Teflon bottle.

6. Procedure

6.1 Place 400-ml aliquots of the filtered samples in 600-ml beakers. Prepare two standards by addition of 8.0 ml of uranium standard solution III to 400 ml of distilled water in 600-ml beakers. Also prepare a blank of 400 ml of distilled water. An additional blank and standard (prepared by pipetting 50 μl of uranium standard solution II directly into the platinum dish) are taken

through steps 6.11 through 6.19 of this procedure.

6.2 Add 3 ml of concentrated HNO_3 , 1 ml of 0.2 M aluminum nitrate reagent, and 5 ml of 0.090 M diammonium-hydrogen phosphate reagent. Heat to boiling to remove carbon dioxide.

6.3 Add a few drops of methyl red indicator, and neutralize just to the yellow endpoint by dropwise additions of concentrated ammonium hydroxide with constant stirring. If, on addition of the indicator, a pink color forms and then disappears, the water probably contains an excessive amount of iodide or bromide ions. In that event, add ammonium hydroxide, 2 or 3 drops at a time; then add a drop of indicator. Repeat this procedure until the indicator exhibits the yellow color instantly upon hitting the solution.

6.4 Digest the precipitate near the boiling point on a hotplate or steam bath for 30 min; then allow to cool to room temperature and settle.

6.5 Using a small pipet connected to an aspirator, draw off as much of the supernate as possible without disturbing the precipitate.

6.6 Transfer the precipitate to a 40- or 50-ml screw-cap Pyrex centrifuge tube. Polish the beaker and the stirring rod with 1 percent ammonium nitrate solution, adding the washings to the centrifuge tube. Centrifuge, discard the supernate, and add 4 or 5 ml of the 1-percent ammonium nitrate solution. Agitate the mixture in the tube to wash the precipitate, and again centrifuge and discard the supernate. Note: In transferring the precipitate to the centrifuge tube it will probably be necessary to centrifuge and decant once before the transfer can be completed.

6.7 Oven-dry the precipitate in the centrifuge tube for 15-20 minutes at 80°C. Raise oven temperature to approximately 100°C and take to complete dryness.

6.8 Add 8 ml of the $\text{Mg}(\text{NO}_3)_2$ reagent, and warm gently to dissolve the precipitate. Use the ultrasonic generator to speed dissolution.

6.9 When cool, add 10 ml of cold ethyl ether to the test tube, cap, and agitate vigor-

ously for at least 2 min. Allow about 15 min for the two layers to separate.

6.10 Pipet off 5.0 ml of the ethyl ether layer using a 5-ml pipet with a control, and place in a 125-ml Teflon dish to which approximately 8 drops of water have been added. Add another 5 ml of ether to the tube, cap, and agitate for 2 min. Again, allow 15 min for the layers to separate, then pipet an additional 5 ml of the ethyl ether layer from the tube into the same Teflon dish. Use the ultrasonic generator to break up emulsions. The equivalent volume transferred is thus 7.5 ml of the original 10 ml of ether added.

6.11 Allow the ethyl ether to evaporate completely in a fume hood at room temperature. Heat gently on a hotplate to complete dryness.

6.12 Transfer the sample from the Teflon evaporating dish to the platinum dish used for fusion with a small portion of ethyl alcohol, policing the bottom and the sides of the Teflon dish thoroughly with a small rubber policeman. Repeat the ethyl alcohol wash one more time. A third wash must be completed using a small portion of distilled water. Combine with the ethyl alcohol washes immediately. The three washes must be kept small enough so the combined washes do not exceed the volume of the platinum fusion dish. (Here again the distilled water wash serves a double purpose: (1) assures complete transfer of the sample, and (2) reduces the ethyl alcohol creep up the sides of the fusion dish.) Take fusion dish to dryness under a heat lamp.

6.13 Carefully flame fusion dish over a burner until the dish is a dull red.

6.14 Add 2 g of flux and prepare fluorescent disk as in method R-1180-76.

6.15 Place the dishes in a desiccator, and cool for at least 30 min. Determine the fluorescence of the samples, blank, and standard as in method R-1180-76.

7. Calculations

Concentration of uranium is calculated from the equation:

$$\mu\text{g/l of U} = \frac{1,000 S(A-B)}{V(C-B)} \frac{R_n}{R_s},$$

where

S = μg of uranium added to prepare the standards,

A = mean fluorimeter reading of the sample disks,

B = mean fluorimeter reading of the blank disks,

C = mean fluorimeter reading of the standard disks,

V = volume of the sample in milliliters,

R_s = fractional recovery of uranium extracted from the sample, and

R_n = fractional recovery of uranium extracted from the standard.

The fraction of uranium recovered in serial extraction of the samples and standards (R_s, R_n) is determined by equation:

$$R = \frac{v_1}{V_1} + 1 \left(\frac{v_1}{V_1} \right) \left(\frac{v_2}{V_2} \right) + 1 \left[-\frac{v_1}{V_1} - \left(1 - \frac{v_1}{V_1} \right) \left(\frac{v_2}{V_2} \right) \left(\frac{v_3}{V_3} \right) + \dots \right] \left(\frac{v_4}{V_4} \right),$$

where

v = volume of ether (ml) removed after each extraction, and

V = volume of ether (ml) in the sample for each extraction.

When V is equal to 10 ml and v is equal to 5 ml (normal procedure) the R values for the first, second, third, and fourth extractions are respectively 0.5, 0.75, 0.875, and 0.937.

When the serial extraction of the sample is identical to the serial extraction of the standard (same number of extractions using the same volumes) the fractional recoveries cancel and the equation simplifies to:

$$\mu\text{g/l of U} = \frac{1,000 S(A-B)}{V(C-B)}.$$

8. Report

Report concentrations to two significant figures above 0.10 $\mu\text{g/l}$ and to one significant figure for values below 0.10 $\mu\text{g/l}$ with 0.01 $\mu\text{g/l}$ as the minimum.

9. Precision

Minimum detectable concentration is 0.01 $\mu\text{g/l}$. The precision of the fluorescence methods for determination of uranium is governed primarily by conditions in the flux and in the fusion operation. Reproducibility of the fluorescence from replicates standards averages ± 15 percent. The same value is used for precision of sample runs except at concentrations below approximately 0.07 $\mu\text{g/l}$ where $\pm \text{MDL}$ represents the precision.

References

- Barker, F. B., Johnson, J. O., Edwards, K. W., and Robinson, B. P., 1965, Determination of uranium in natural waters: U.S. Geol. Survey Water-Supply Paper 1696-C, 25 p.
- Hellman, N. N., and Wolfe, M. J., 1952, Influence of various nitrates on the diethyl ether extraction of low concentrations of uranium from thorium, *in* Production and Separation of Uranium-233 (ed., L. Katzin): U.S. Atomic Energy Comm. TID 5223, pt. 1.
- Smith, A. P., and Grimaldi, F. S., 1954, The fluorimetric determination of uranium in nonsaline and saline waters, *in* Collected papers on methods of analysis for uranium and thorium: U.S. Geol. Survey Bull. 1006, p. 125-131.

Uranium, dissolved, isotopic ratios

Alpha spectrometry—chemical separation (R-1182-76)

**Parameter and code: Uranium, dissolved, isotope ratio (dimensionless):
none assigned**

1. Application

The method is applicable to most fresh-water and saline waters. Industrial wastes and mine drainage may require special treatment.

2. Summary of method

The uranium isotopes are determined by alpha spectrometry after concentration and separation from the bulk of the water sample by use of the precipitation-extraction procedure described under method R-1181-76 determination of uranium. This is followed by an ion-exchange procedure to eliminate thorium, an alpha-emitting radionuclide. The final step is electrodeposition of the uranium (as uranium oxide) in a very thin layer on a metal disk. Electrodeposition conditions are critical because thick or non-uniform deposition must be avoided, and interfering radioisotopes must be kept in the solution phase. Thick or nonuniform electrodepositions result in distortion of the alpha energy peaks and reduced counting efficiency. The procedure is described in detail by Edwards (1968).

Alpha spectroscopy is carried out by means of a silicon surface-barrier detector with output to a linear amplifier and multi-channel analyzer. Readout is by means of an x-y plotter and electric typewriter which prints out counts in each energy channel.

The alpha spectra of the uranium isotopes are as follows:

Uranium-238; 4.195 MeV (0.77), 4.147 MeV (0.23)
Uranium-235; 4.370 MeV (0.25), 4.354 MeV (0.35),
(with five other energy peaks of less intensity)
Uranium-234; 4.768 MeV (0.72), 4.717 MeV (0.28).

Since surface-barrier detectors can be obtained with resolution as fine as 0.030 MeV (30 keV) (for 450 mm² counting area), it is possible to cleanly resolve all the uranium peaks of interest.

Because of the very low radioactivity of uranium, it may be necessary to collect the uranium from a relatively large water sample to yield between 2.5 and 220 μg of uranium. Samples as large as 25 liters can be used.

3. Interferences

There is no direct spectral overlap by other natural alpha-emitting nuclides. However, if thorium-230 or protoactinium-231 are present in great excess, broadening of their peaks might introduce a small error. Transition metals, when present in great excess, might be carried through the final electrodeposition to increase the mass of the deposit. This would broaden the alpha energy peaks and reduce the counting efficiency. None of these possible adverse effects have yet been encountered in practice.

4. Apparatus

4.1 *Detector*, silicon surface-barrier detector with approximately 450 mm² sensitive area and depletion depth of 60 microns or more.

4.2 *Vacuum chamber*. The detector is mounted in a chamber which is evacuated

after the sample is inserted. This is essential to minimize scattering of alphas by air. A vacuum pump and silica-gel moisture trap are used to maintain vacuum at 0.1 torr.

4.3 *Multichannel analyzer array.* The signal is fed from the detector through a pre-amplifier and linear amplifier into a multichannel analyzer where the alpha energy pulses are routed to their appropriate channels in the memory. The analyzer should have a minimum of 256 channels if the full resolution capability of the best silicon barrier detectors is to be realized.

4.4 *Readout system.* The memory may be read out using a plotter, teletype unit, punched tape, magnetic tape, or other appropriate means. The combination of x-y plotter and electric typewriter has been found to be satisfactory.

4.5 *Chemical-separation apparatus.* The chemical apparatus required for method R-1181-76 (items 4.6 to 4.8) are used.

4.6 *Ion-exchange columns.* These are designed to hold 40 ml of liquid in a funnel top and to pass the solution through a 14-cm length of ion-exchange resin, 1 cm in diameter.

4.7 *Electrolysis apparatus.* The cell is designed to plate a circular deposit 2.2 cm in diameter to correspond with the sensitive diameter of the alpha detector. The deposit is collected on a titanium disk which is clamped onto the bottom of a Teflon cylinder thus forming an electrolysis cup. The titanium disk is the cathode. The anode is a flat coil of platinum wire suspended 2.2 cm above the titanium disk. Power is supplied by a small 12-volt rectifier with voltmeter and ammeter. The titanium disks are 3.2 cm in diameter.

5. Reagents

5.1 *Electroplating reagents,* NH_4Cl solution, 2 N; acetone; and ammonia.

5.2 *Ion-exchange reagents,* Bio-Rad AG 1-X8, 50-100 mesh or equivalent. Hydrochloric acid, 8 N and 0.1 N.

5.3 *Precipitation-extraction reagents.* All reagents required for the precipitation-extraction steps of method R-1181-76 are used.

6. Procedure

6.1 Determine the volume of sample required by carrying out the fluorimetric uranium analysis by method R-1180-76 or R-1181-76 as indicated by the nature of the sample. The maximum weight of uranium that can be used in the isotopic analysis is 220 μg and the minimum is 2.5 μg . Recommended sample volumes for a thousandfold range of uranium concentrations are given in table 2.

Table 2.—Recommended sample volumes, minimum, and reduced volumes for isotopic uranium analysis

U concentration ($\mu\text{g}/\text{l}$)	Volume, in liters		
	Recommended	Minimum	Reduced volume
0.10 -----	25	25	5
.2 -----	25	12.5	5
.3 -----	25	8.4	5
.4 -----	20	6.3	4
.5 -----	20	5.0	4
.6 -----	20	4.2	4
.8 -----	20	3.2	4
1.0 -----	20	2.5	4
1.2 -----	20	2.1	4
1.5 -----	20	1.7	4
2.0 -----	15	1.25	3
3.0 -----	10	.84	2
5.0 -----	10	.50	2
7.0 -----	5	.36	1
10 -----	5	.25	1
12 -----	5	.21	1
15 -----	5	.17	1
20 -----	2	.13	1
30 -----	2	.084	1
50 -----	2	.050	1
70 -----	1	.036	1
100 -----	1	.025	1

6.2 If the sample volume exceeds 1 liter, evaporate on a hotplate to the reduced volume value shown in table 2. If the reduced volume exceeds 1 liter it is necessary to divide the sample into two or more 1-liter portions. Each portion is carried through the procedure as an individual sample through step 6.3. Run a blank of 1-liter distilled water through the procedure.

6.3 Carry out the uranium extraction procedure, method R-1181-76, steps 6.2 through 6.11. If two or more 1-liter portions of one sample are extracted, combine the extracts before step 6.11.

6.4 Dissolve the dry residue that remains from the evaporation of the ether layer in 10 ml of 8 N HCl.

6.5 Prepare the ion-exchange columns by washing 6 g of resin in a beaker with 8 N HCl. Transfer to the columns and wash with 8 N HCl.

6.6 Pour the solution from 6.3 into the ion-exchange tube. Allow to flow through at the rate of 20–30 drops per minute. Elute thorium with 50 ml of 8 N HCl and discard this eluate. Elute uranium with 60 ml of 0.1 N HCl.

6.7 After evaporating to dryness, adding HNO₃, and evaporating again to eliminate the last traces of HCl, prepare the residue for electrolysis by dissolving in the electrolyte, 10 ml of 2 N NH₄Cl.

6.8 Transfer to the electrolysis cell, and plate the uranium onto the titanium disk using current of 1 ± 0.1 ampere. Electrolyze for 100 min.

6.9 Introduce the dry sample on the titanium disk into the vacuum chamber, pump down to 0.1 torr, and count the alpha activity of the sample for 1,000 min using the energy range 3.8–5.3 MeV.

6.10 Printout the spectrum with the x–y plotter and the typewriter.

7. Calculations

7.1 Identify the uranium isotopes present on the basis of the x–y plot, using the data from the typed readout, establish the count under the principal alpha energy peak for each isotope by summing the counts and subtracting the blank. Since background for the samples and the blank is the same when nor-

malized to the same counting time, this also corrects for background.

The isotopic ratio is:

$$R = \frac{U-234}{U-238} = \frac{C-234}{C-238},$$

where

C–234 = counts under the 4.763 MeV peak corrected for blank, and

C–238 = counts under the 4.195 MeV peak corrected for blank.

7.2 Determine concentration of each uranium isotope, if desired, by applying the isotope ratio to the concentration of total uranium as determined by fluorescence method R–1180–76 or R–1181–76.

8. Report

Report activity ratios less than one to two significant figures. Report activity ratios greater than one to three significant figures.

9. Precision

There are insufficient data to establish a reliable experimental standard deviation. Standard deviation based on counting statistics may be calculated using the following:

$$\sigma = R \left(\frac{(C-234) + B + 1}{((C-234) - B)^2} + \frac{(C-238) + B + 1}{((C-238) - B)^2} \right)^{1/2},$$

where

B = experimentally determined blank.

Derivation of the equation may be found in Edwards (1968).

Reference

Edwards, K. W., 1968, Isotopic analysis of uranium in natural waters by alpha spectrometry: U.S. Geol. Survey Water-Supply Paper 1696–F, 26 p.