METHOD 9320

RADIUM 228

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed standard operating procedure (SOP), either for its own general use or for a specific project application. Performance data included in this method are for guidance purposes only and must not be used as absolute quality control (QC) acceptance criteria for purposes of laboratory QC or accreditation.

1.0 SCOPE AND APPLICATION

Please see Appendix A at the back of this document for a summary of revisions to Method 9320 (From Revision 0, September 1986).

1.1 This method covers the measurement of radium-228 in ground water and, if desired, the determination of radium-226 on the same sample. If the level of radium-226 is above 3 pCi/L, the sample must also be measured for radium-228.

1.2 This technique is devised so that the beta activity from actinium-228, which is produced by decay of radium-228, can be determined and related to the radium-228 that is present in the sample.

1.3 To quantify actinium-228 and thus determine radium-228, the efficiency of the beta counter for measuring the very short half-lived actinium-228 (avg. beta energy of 0.404 keV) is to be calibrated with a beta source of comparable average beta energy.

1.4 Analysts should consult the disclaimer statement at the front of the manual and the information in Chapter Two for 1) guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies; 2) the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by the Environmental Protection Agency (EPA) as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.5 This method is restricted to use by, or under supervision of, properly experienced and trained personnel. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

The radium in the water sample is collected by coprecipitation with barium and lead sulfate and purified by reprecipitation from EDTA solution. Both radium-226 and radium-228 are collected in this manner. After a 36-hr ingrowth of actinium-228 from radium-228, the actinium-228 is carried on yttrium oxalate, purified and beta counted. If radium-226 is also desired, the activity in the supernatant can be reserved for coprecipitation on barium sulfate, dissolving in EDTA and storing for ingrowth in a sealed radon bubbler.

3.0 DEFINITIONS

Refer to Chapter One, Chapter Three, and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences during sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents may be necessary. Refer to Chapter Three for general guidance on glassware cleaning.

4.2 As evidenced by the results of the performance studies, the presence of strontium-90 in the water sample gives a positive bias to the radium-228 activity measured. However, strontium-90 is not likely to be found in ground water, except possibly in monitoring wells around a radioactive burial site.

4.3 Excess barium in the water sample might result in a falsely high chemical yield.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2 Personal protective equipment (PPE) should be worn at all times when in the laboratory. PPE requirements include chemical splash goggles and protective clothing and gloves.

5.3 Acetic acid can cause severe skin and eye burns. The liquid and vapors are flammable. Carefully follow handling and storage instructions found in its MSDS.

5.4 Ammonium hydroxide is corrosive; carefully follow handling and storage instructions found in its MSDS.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list all common laboratory glassware (e.g., beakers and flasks) that might be used.

6.1 Gas-flow proportional counting system (low-background beta <3 cpm).

6.2 Electric hot plate.

6.3 Centrifuge.

6.4 Membrane filters: Matricel 47-mm.

6.5 Drying lamp.

6.6 Stainless steel counting planchets.

6.7 Analytical balance.

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade chemicals, at a minimum, should be used in all tests. Unless otherwise indicated, all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Reagent water -- Reagent water must be interference free. All references to water in this method refer to reagent water unless otherwise specified.

7.3 Acetic acid (17.4 N), glacial CH_3COOH (concentrated) sp. gr. 1.05, 99.8%.

7.4 Ammonium hydroxide (15 N), NH_4OH (concentrated) sp. gr. 0.90, 56.6%.

7.5 Ammonium oxalate (5%): Dissolve 5 g $(NH_4)_2C_2O_4 \cdot H_2O$ in reagent water and dilute to 100 mL.

7.6 Ammonium sulfate (200 mg/mL): Dissolve 20 g $(NH_4)_2SO_4$ in reagent water and dilute to 100 mL.

7.7 Ammonium sulfide (2%): Dilute 10 mL $(NH_4)_2S$ (20-24%), to 100 mL with reagent water.

7.8 Barium carrier (16 mg/mL), standardized: Dissolve 2.846 g $BaCl_2 \cdot 2H_2O$ in reagent water, add 0.5 mL 16 N HNO_3, and dilute to 100 mL with Type II water.

7.9 Citric acid (1 M): Dissolve 19.2 g $C_6H_8O_7 \cdot H_2O$ in reagent water and dilute to 100 mL.

7.10 EDTA reagent, basic (0.25 M): Dissolve 20 g NaOH in 750 mL reagent water, heat, and slowly add 93 g disodium ethylenedinitriloacetate dihydrate ($Na_2C_{10}H_{14}O_8N_2 \cdot 2H_2O$) while stirring. After the salt is in solution, filter through coarse filter paper, and dilute to 1 liter.

7.11 Lead carrier (15 mg/mL): Dissolve 2.397 g $Pb(NO_3)_2$ in reagent water, add 0.5 mL 16 N HNO_3, and dilute to 100 mL with reagent water.

7.12 Lead carrier (1.5 mg/mL): Dilute 10 mL lead carrier (15 mg/mL) to 100 mL with reagent water.

7.13 Standard strontium-89 tracer solution.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Sample collection, preservation, and storage requirements may vary by EPA program and may be specified in a regulation or project planning document that requires compliance monitoring for a given contaminant. Where such requirements are specified in the regulation, follow those requirements. In the absence of specific regulatory requirements, use the following information as guidance in determining the sample collection, preservation, and storage requirements.

8.1 All samples must have been collected in a manner which addresses the considerations discussed in Chapter Nine of the SW-846 manual.

8.2 It is recommended that samples be preserved at the time of collection by adding enough 1 N HNO_3 to the sample to bring it to pH 2 (15 mL 1 N HNO_3 per liter of sample is usually sufficient). If samples are to be collected without preservation, they should be brought to the laboratory within 5 days, then preserved, and held in the original container for a minimum of 16 hr before analysis or transfer of the sample. See also Note to Paragraph 7.2 below.

8.3 All sample containers must be prewashed with acids, water, and metal-free detergents, if necessary, depending on the use history of the container. For further information see Chapter Three.

8.4 The container choice should be plastic (rather than glass) to prevent loss due to breakage during transportation and handling.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and QC protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and Chapter One criteria; technique-specific QC criteria take precedence over Chapter One criteria. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results.

Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. Development of in-house QC limits for each method is encouraged. Use of instrument specific QC limits is encouraged, provided such limits will generate data appropriate for use in the intended application. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Initial demonstration of proficiency (IDP).

The initial demonstration of method proficiency must be performed prior to independently running an analytical method, and should be repeated if other changes occur (e.g., instrument repair, significant change in procedure, and change in analyst). An IDP must consist of replicate reference samples from each sample preparation and determinative method combination it utilizes by generating data of acceptable accuracy and precision for target analytes in a clean reference matrix taken through the entire preparation and analysis.

9.3 Sample QC for preparation and analysis

The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, bias, and sensitivity). At a minimum, this should include the analysis of QC samples including a method blank, a matrix spike (MS), a laboratory control sample (LCS), and a duplicate sample in each analytical batch. Any method blanks, LCS, MS samples, and duplicate samples should be subjected to the same preparatory and instrument determination procedures as those used on actual samples (see Sec. 11.0).

10.0 CALIBRATION AND STANDARDIZATION

Counter efficiency: The beta counter may be calibrated with actinium-228 or strontium-89 ($t_{1/2}$ = 51 d). Strontium-89 has an average beta energy of 0.589 KeV. A standard strontium-89 tracer solution can be used to determine beta efficiencies over a range of precipitate weights on the stainless steel planchet.

11.0 PROCEDURE

11.1 For each liter of water add 5 mL 1 M $C_6H_8C_7 \bullet H_2O$ and a few drops of methyl orange indicator. The solution should be red.

NOTE: At the time of sample collection add 2 mL 16 N HNO_3 for each liter of water.

11.2 Add 10 mL lead carrier (15 mg/mL), 2 mL strontium carrier (10 mg/mL), 2.0 mL barium carrier (16 mg/mL), 1 mL yttrium carrier (18 mg/mL) and stir well. Add 15 N NH_4OH until a definite yellow color is obtained; then add a few drops excess. Heat to incipient boiling and maintain at this temperature for 30 min.

11.3 Precipitate lead and barium sulfates by adding 18 N H_2SO_4 until the red color reappears. Then add 0.25 mL excess. Add 5 mL $(NH_4)_2SO_4$ (200 mg/mL) for each liter of sample. Stir frequently and keep at a temperature of about 90°C for 30 min.

11.4 Cool slightly; then filter with suction through a 47-mm matricel membrane filter (GA6, 0.45-micron pore size). Make a quantitative transfer of precipitate to the filter by rinsing last particles out of beaker with a strong jet of water.

11.5 Carefully place filter with precipitate in the bottom of a 250-mL beaker. Add about 10 mL 16 N HNO_3 and heat gently until the filter completely dissolves. Transfer the precipitate into a polypropylene centrifuge tube with an additional 16 N HNO_3. Centrifuge and discard supernatant.

11.6 Wash the precipitate with 15 mL 16 N HNO_3, centrifuge, and discard supernatant. Repeat this washing a second time.

11.7 Wash the precipitate with 10 mL reagent water, centrifuge, and discard supernatant.

11.8 Add 25 mL basic EDTA reagent, heat in a hot-water bath, and stir well. Add a few drops 10 N NaOH if the precipitate does not readily dissolve.

11.9 Add 1 mL strontium-yttrium mixed carrier and stir thoroughly. Add a few drops 10 N NaOH if any precipitate forms.

11.10 Add 1 mL $(NH_4)_2SO_4$ (200 mg/mL) and stir thoroughly. Add 17.4 N acetic acid until the barium sulfate precipitates. Then add 2 mL excess. Digest in a hot water bath until precipitate settles. Centrifuge and discard supernatant.

11.11 Add 20 mL basic EDTA reagent, heat in a hot-water bath, and stir until precipitate dissolves. Repeat steps 7.9 and 7.10. (Note time of last barium sulfate precipitation as this is the beginning of the actinium-228 ingrowth time.)

11.12 Dissolve the precipitate in 20 mL basic EDTA reagent as before; then add 1.0 mL yttrium carrier (9 mg/mL) and 1 mL lead carrier (1.5 mg/mL). If any precipitate forms, dissolve by adding a few drops 10 N NaOH. Cap the polypropylene tube and age at least 36 hr.

11.13 Add 0.3 mL $(NH_4)_2S$ and stir well. Add 10 N NaOH dropwise with vigorous stirring until lead sulfide precipitates. Then add 10 drops excess. Stir intermittently for about 10 min. Centrifuge and decant supernatant into a clean tube.

11.14 Add 1 mL lead carrier (1.5 mg/mL), 0.1 mL $(NH_4)_2S$ and a few drops 10 N NaOH. Repeat precipitation of lead sulfide as before. Centrifuge and filter supernates through Whatman #42 filter paper into a clean tube. Wash filter with a few mL water. Discard residue.

11.15 Add 5 mL 18 N NaOH, stir well and digest in a hot water bath until yttrium hydroxide coagulates. Centrifuge and decant supernates into a beaker. Save for barium yield determination (step 7.20). (Note time of yttrium hydroxide precipitation as this is the end of the actinium-228 ingrowth time and beginning of actinium-228 decay time.)

11.16 Dissolve the precipitate in 2 mL 6 N HNO_3. Heat and stir in a hot water bath about 5 min. Add 5 mL water and re-precipitate yttrium hydroxide with 3 mL 10 N NaOH. Heat and stir in a hot water bath until precipitate coagulates. Centrifuge and add this supernate to the supernate produced in step 7.15 in order to determine barium yield.

11.17 Dissolve precipitate with 1 mL 1 N HNO_3 and heat in hot water bath a few minutes. Dilute to 5 mL and add 2 mL 5% $(NH_4)_2C_2O_4 \cdot H_2O$. Heat until mixture coagulates, then centrifuge and discard supernatant.

11.18 Add 10 mL water, 6 drops 1 N HNO_3 and 6 drops 5% $(NH_4)_2C_2O_4 \cdot H_2O$. Heat and stir in a hot-water bath a few minutes. Centrifuge and discard supernatant.

11.19 To determine yttrium yield, transfer quantitatively to a tared stainless steel planchet with a minimum amount of water. Dry under an infrared lamp to a constant weight and count in a low-background beta counter.

11.20 To the supernatant from step 7.15, add 4 mL 16 N HNO_3 and 2 mL $(NH_4)_2SO_4$ (200 mg/mL), stirring well after each addition. Add 17.4 N acetic acid until barium sulfate precipitates. Then add 2 mL excess. Digest on a hot plate until precipitate settles. Centrifuge and discard supernatant.

11.21 Add 20 mL basic EDTA reagent, rest in a hot-water bath, and stir until precipitate dissolves. Add a few drops 10 N NaOH if precipitate does not readily dissolve.

11.22 Add 1 mL $(NH_4)_2SO_4$ (200 mg/mL) and stir thoroughly. Add 17.4 N acetic acid until barium sulfate precipitates. Then add 2 mL excess. Digest in a hot-water bath until precipitate settles. Centrifuge and discard supernatant.

11.23 Wash precipitate with 10 mL water. Centrifuge and discard supernatant.

11.24 Transfer precipitate to a tared stainless steel planchet with a minimum amount of water. Dry under an infrared lamp and weigh for barium yield determination.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Results need to be reported in units commensurate with their intended use and all dilutions need to be taken into account when computing final results.

12.2 Calculate the radium-228 concentration, D, in picocuries per liter as follows:

$$\mathrm{D} = \frac{\mathrm{C}}{2.22 \times \mathrm{EVR}} \times \frac{\lambda t_2}{(1 - e^{-\lambda t_2})} \times \frac{1}{(1 - e^{-\lambda t_3})} \times \frac{1}{(e^{-\lambda t_1})}$$

<u>NOTE</u>: $\frac{\lambda t_2}{(1-e^{-\lambda t_2})}$ is a factor to correct the average count rate to the count rate at the beginning of counting time.

where:

C = Average net count rate, cpm;

E = Counter efficiency, for actinium-228, or comparable beta energy nuclide;

V = Liters of sample used;

R = Fractional chemical yield of yttrium carrier (Step 11.18) multiplied by fractional chemical yield of barrier carrier (Step 11.23);

2.22 = Conversion factor from disintegrations/minute to picocuries;

λ = The decay constant for actinium-228 (0.001884 min^{-1});

t_1 = The time interval (in min) between the first yttrium hydroxide precipitation in Step 11.14 and the start of the counting time;

t_2 = The time interval of counting in min; and

t_3 = The ingrowth time of actinium-228 in min measured from the last barium sulfate precipitation in Step 11.10 to the first yttrium hydroxide precipitation in Step 11.14.

13.0 METHOD PERFORMANCE

Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. <u>Performance data must not be used as absolute QC acceptance criteria for laboratory QC or accreditation.</u>

Performance data examples and guidance for this method currently are not currently available.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction*, a free publication available from the American Chemical Society (ACS), Committee on Chemical Safety, http://portal.acs.org/portal/fileFetch/C/WPCP_012290/pdf/WPCP_012290.pdf.

15.0 WASTE MANAGEMENT

The EPA requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. Laboratories are urged to protect air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the ACS at the address listed in Sec. 14.2.

16.0 REFERENCES

1. A.E. Greenberg, J.J. Connors, and D.J. Jenkens, eds., Standard Methods for the Examination of Water and Wastewater, 15th ed., American Public Health Assoc., Washington, D.C., Method 707, p. 600, 1980.

2. J.O. Johnson, Determination of Radium 228 in Natural Waters. Radiochemical Analysis of Water. U.S. Geol. Surv., Water Supply Paper 1696-G. U.S. Govt. Printing Office, Washington, D.C., 1971.

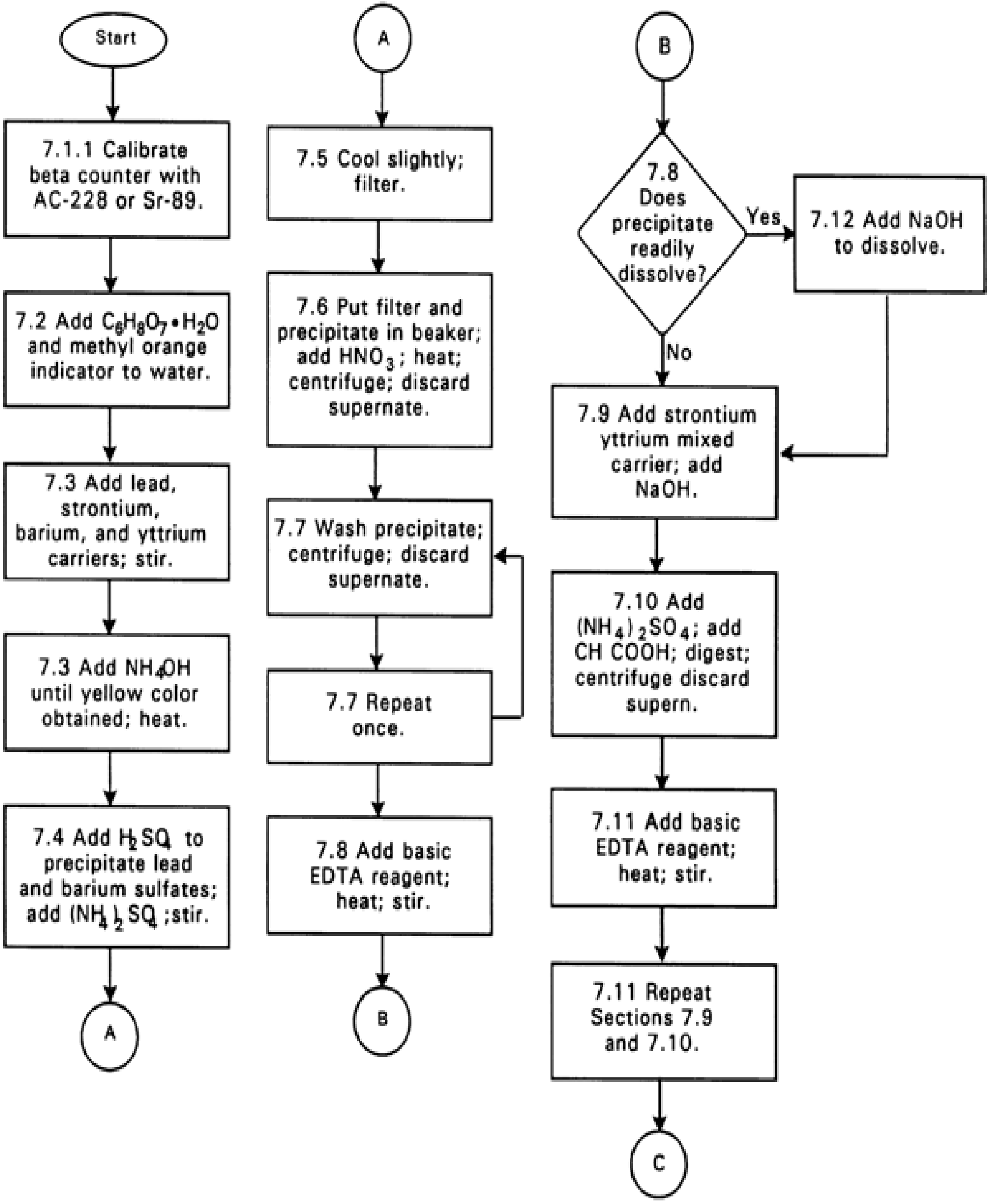
3. H.L. Krieger, Prescribed Procedures for Measurement of Radioactivity in Drinking Water, Environmental Monitoring and Support Laboratory, U.S. EPA, Cincinnati, OH, EPA-600/4-75-008, 1976.

17.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

The following pages contain figures that provide illustration for the procedures of this method.

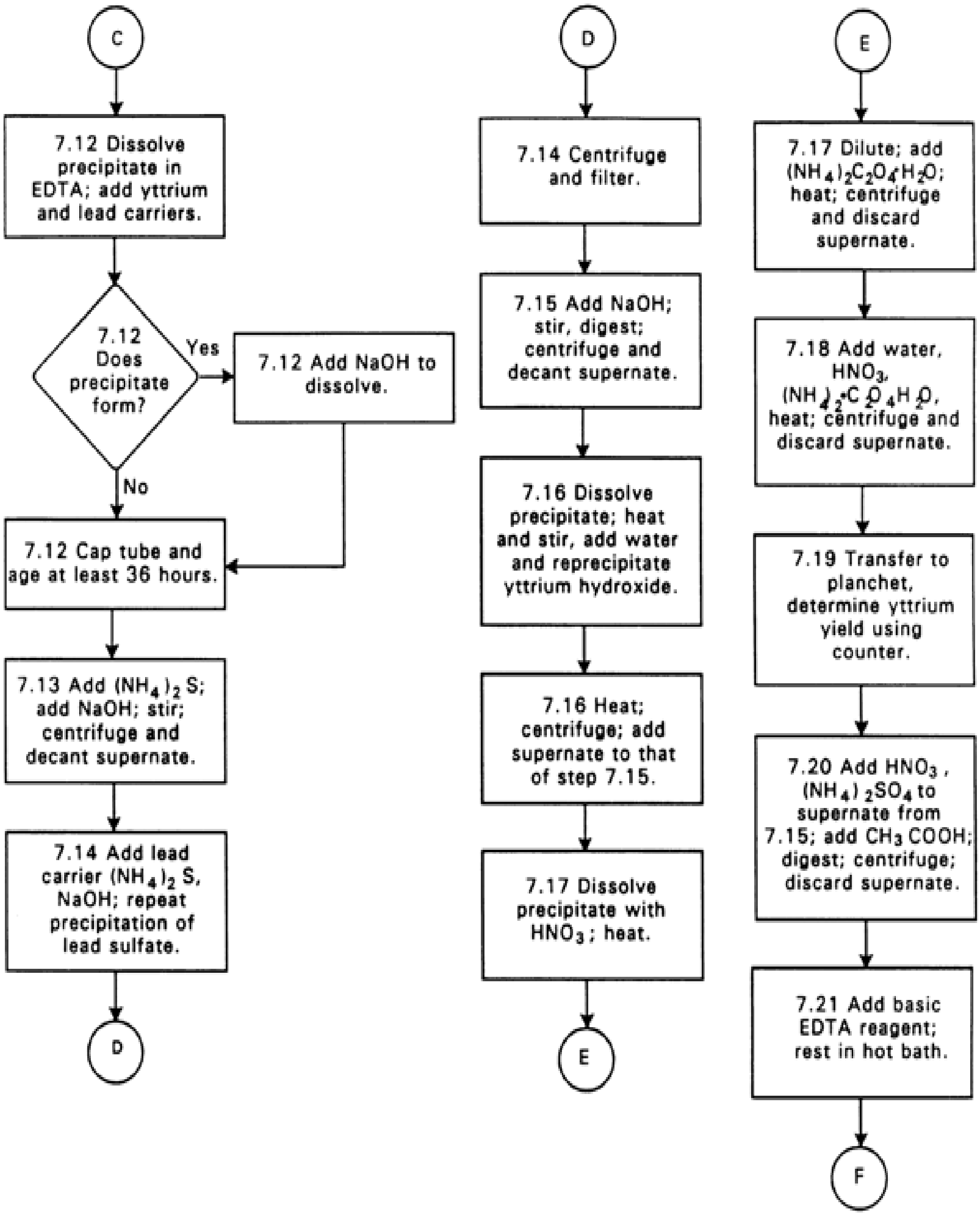
METHOD 9320

RADIUM-228

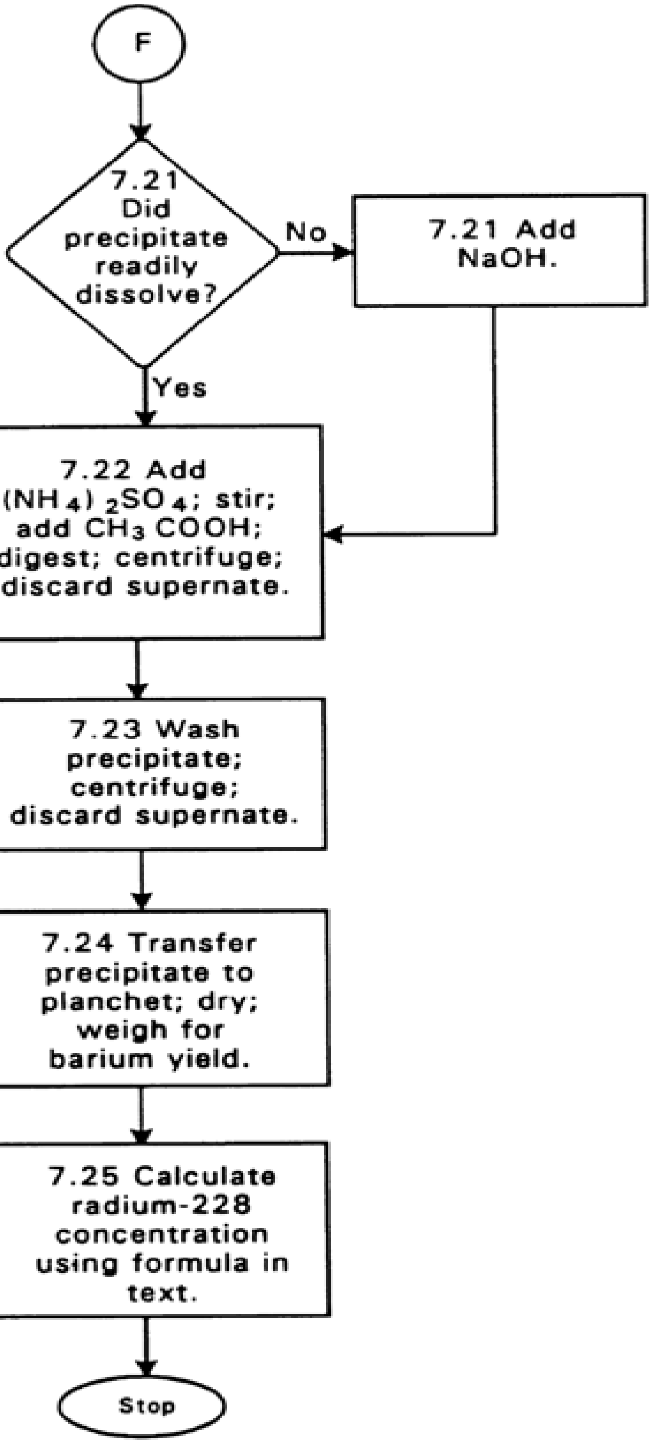


METHOD 9320

RADIUM-228



RADIUM-228


F
7.21 Did precipitate readily dissolve?
No
7.21 Add NaOH.
Yes
7.22 Add $(NH_4)_2SO_4$; stir; add CH_3COOH; digest; centrifuge; discard supernate.
7.23 Wash precipitate; centrifuge; discard supernate.
7.24 Transfer precipitate to planchet; dry; weigh for barium yield.
7.25 Calculate radium-228 concentration using formula in text.
Stop

Appendix A

Summary of Revisions to Method 9320 (From Revision 0, September 1986)

1. Improved overall method formatting for consistency with new SW-846 methods style guidance.
2. Extensively reformatted "REAGENTS AND STANDARDS" section and to meet current SW-846 method guidelines.
3. Updated and expanded "QUALITY CONTROL" section for better adherence to current SW-846 method guidelines and for improved alignment with current universal practices for published analytical methods.
4. In Section 9.2, the recommendation of an initial demonstration of proficiency for analysts and instrumentation and/or procedure changes was added.
5. The Section 11.7 was added; instructing a reagent water wash after the two HNO_3 washes in Sec. 11.6. This step will help prevent and reduce interferences later in the procedures and analysis.
6. The revision number was changed to one and the date published to July 2014.