



Designation: D7535 – 09<sup>ε1</sup>

## Standard Test Method for Lead-210 in Water<sup>1</sup>

This standard is issued under the fixed designation D7535; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

<sup>ε1</sup> NOTE—Added research report footnote to Section 15 editorially in June 2013.

### 1. Scope

1.1 This test method covers the determination of radioactive <sup>210</sup>Pb in environmental water samples (for example, drinking, non-process and effluent waters) in the range of 37 mBq/L (1.0 pCi/L) or greater.

1.2 The values stated in SI units are to be regarded as standard. The values given in parentheses are provided for information purposes only.

1.3 This method has been used successfully with tap water. It is the user's responsibility to ensure the validity of this test method for samples larger than 500 mL and for waters of untested matrices.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. For specific hazards statements, see Section 9.*

### 2. Referenced Documents

- 2.1 *ASTM Standards:*<sup>2</sup>
- D1129 Terminology Relating to Water
  - D1193 Specification for Reagent Water
  - D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
  - D3370 Practices for Sampling Water from Closed Conduits
  - D4448 Guide for Sampling Ground-Water Monitoring Wells
  - D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
  - D6001 Guide for Direct-Push Groundwater Sampling for Environmental Site Characterization
  - D7282 Practice for Set-up, Calibration, and Quality Control

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.04 on Methods of Radiochemical Analysis.

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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

of Instruments Used for Radioactivity Measurements  
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

### 3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D1129.

### 4. Summary of Test Method

4.1 This test method is based on the utilization of solid phase extraction of lead from water samples with detection of the radioactive lead by beta gas flow proportional counting. An aliquot of the sample is measured into a beaker; iron carrier and lead carrier are added. Lead is scavenged by an iron hydroxide precipitation. Lead is then selectively sorbed on a solid phase extraction column and eluted with water. Lead is precipitated as lead sulfate and is collected on a filter paper. The lead sulfate precipitate is covered with aluminum foil and held for 5 days or longer for <sup>210</sup>Bi ingrowth. It is then counted for beta radiation on a gas flow proportional counter.

### 5. Significance and Use

5.1 This test method was developed to measure the concentration of <sup>210</sup>Pb in nonprocess water samples. This test method may be used to determine the concentration of <sup>210</sup>Pb in environmental samples.

### 6. Interferences

6.1 Significant amounts of stable lead (>0.3 mg/L) present in the sample will interfere with the chemical yield determination, leading to positive bias in the yield. If it is known or suspected that natural lead is present in the sample, blank sample aliquots to which no lead carrier content is added should be analyzed. The amount of natural lead contained in the sample shall be used to correct the yield.

6.2 In most cases measurable amounts of <sup>210</sup>Pb will be present in the Pb carrier used in Section 12.1. This additional contribution to the measured sample activity must be determined and treated as additional background activity. For each new carrier solution, the inherent <sup>210</sup>Pb in the carrier must be measured. A brief description of this additional background calibration is given in Section 11.2. Accurate determination of

the combined standard uncertainty and the minimum detectable concentration should include this additional activity in the method background count rate.

6.3 Previous experimental data suggests that barium concentrations of approximately 30 ppm can be a source of interference, leading to chemical yield determinations that may be non-representative and outside normal acceptance criteria.

## 7. Apparatus

### 7.1 Analytical Balance, 0.0001 g.

NOTE 1—A thickness of aluminum of approximately 0.003 in. (areal density of approximately 0.02 mg/cm<sup>2</sup>) is needed to effectively eliminate the 60 keV beta particles from <sup>210</sup>Pb.<sup>3</sup> The thickness of aluminum foil used during calibration of the detector and measurement samples must be held constant to maintain self-absorption of <sup>210</sup>Pb and <sup>210</sup>Bi beta particles at a constant level.

### 7.2 Aluminum foil.

### 7.3 Centrifuge.

### 7.4 Centrifuge tubes (50 mL plastic).

7.5 Filters, 25 mm polypropylene, 0.1 μm, with polycarbonate base and metal screen.

7.6 Filter apparatus, polysulfone funnel and 100 mL polypropylene flask.

7.7 Beta Gas Flow Proportional Counting System, (<1.0 cpm beta), low background.

### 7.8 Glass stir rods.

### 7.9 Glass beakers.

### 7.10 Hot plate.

### 7.11 Petri dish.

7.12 Planchets, stainless steel, flat, with diameter large enough to hold the 25 mm filter.

### 7.13 Tweezers.

### 7.14 Watch glass.

## 8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall 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 that the reagent is of sufficiently high purity to permit its use without increasing the background of the measurement. Some reagents, even those of high purity, may contain naturally occurring radioactivity, such as isotopes of uranium, radium, actinium, thorium, rare earths and potassium compounds and/or artificially produced radionuclides. Consequently, when such reagents are used in the analysis of low-radioactivity samples, the activity of the reagents shall be determined under analytical conditions that are identical to those used for the sample. The activity contributed by the

reagents may be considered to be a component of background and applied as a correction when calculating the test sample result. This increased background reduces the sensitivity of the measurement.

8.2 *Purity of water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Specification **D1193**, Type III.

8.3 *Ammonium hydroxide*—15 M NH<sub>4</sub>OH, (concentrated reagent).

8.4 *Iron carrier (20 mg/mL)*—Dissolve 9.6 g of ferric chloride (FeCl<sub>3</sub> · 6H<sub>2</sub>O) in 70 mL of 0.5 M HCl and dilute to 100 mL with 0.5 M HCl.

8.5 *Nitric acid, 16 M HNO<sub>3</sub>*—(concentrated reagent) (sp gr 1.42).

8.5.1 *Nitric acid, 8 M HNO<sub>3</sub>*—Add 500 mL of concentrated nitric acid to 400 mL water. Dilute to 1 L with water and mix well.

8.5.2 *Nitric acid, 1 M HNO<sub>3</sub>*—Add 63 mL of concentrated nitric acid to 800 mL water. Dilute to 1 L with water and mix well.

8.5.3 *Nitric acid, 0.1 M HNO<sub>3</sub>*—Add 6.4 mL of concentrated nitric acid to 600 mL water. Dilute to 1 L with water and mix well.

8.6 *Lead Carrier (10 grams Pb/L)*—Dissolve 1.60 g of lead nitrate in water and dilute to 100 mL with water.

8.7 *Lead Extraction Chromatography column, 2-mL bed volume, 100–150 μm particle size.*<sup>4</sup>

8.8 *Pb-210 Standardizing Solution*—Traceable to a national standardizing laboratory such as National Institute of Standards and Technology, Gaithersburg, MD, USA (NIST) or National Physical Laboratory, Teddington, Middlesex, UK, (NPL) with less than 0.1 mg of stable lead per mL of final solution with a typical <sup>210</sup>Pb concentration range from 85 to 125 Bq/mL. The <sup>210</sup>Pb calibration source should be in equilibrium with its progeny <sup>210</sup>Bi.

8.9 *Sulfuric Acid, 18 M H<sub>2</sub>SO<sub>4</sub>*—concentrated reagent (sp gr 1.84).

## 9. Hazards

9.1 Use extreme caution when handling all acids. They are extremely corrosive, and skin contact could result in severe burns.

9.2 When diluting concentrated acids, always use safety glasses and protective clothing, and add the acid to the water.

## 10. Sampling

10.1 Collect a sample in accordance with Guides **D4448** and **D6001** and Practice **D3370**, or other documented procedure as appropriate.

<sup>3</sup> Radiological Health Handbook, Revised Editions January 1970, Compiled and Edited by the Bureau of Radiological Health and the Training Institute Environmental Control Administration, US Department of Health, Education and Welfare.

<sup>4</sup> Resin available in bulk form and in prepacked columns or cartridges from Eichrom Technologies LLC, Lisle, IL 60532. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,<sup>1</sup> which you may attend.

## 11. Calibration

11.1 *Detection Efficiency Calibration* (see also Practice D7282):

11.1.1 Prepare a set of three working calibration sources according to the calibration procedure outlined in the subsequent steps.

11.1.2 Pipet 1.0 mL of lead carrier into a small beaker.

11.1.3 Add 1.0 mL of <sup>210</sup>Pb standardizing solution to the beaker and evaporate to near dryness on a hot plate at a low setting.

11.1.4 Redissolve the residue in 10 mL of 1 M HNO<sub>3</sub>.

11.1.5 Follow the steps described in 12.9 through 12.28.

11.1.6 Count to amass at least 10 000 counts. Record the time and date of the midpoint of this counting period as  $t_m$ .

11.1.7 *Detection Efficiency Calculation*—Calculate the detection efficiency for <sup>210</sup>Pb for each calibration source and each detector using Eq 1.

$$\varepsilon_{Bi} = \frac{R_a - R_b}{c_s \times V_s \times DF \times IF \times Y_{Pb}} \quad (1)$$

where:

- $\varepsilon_{Bi}$  = detection efficiency for <sup>210</sup>Pb,
- $R_a$  = total count rate (s<sup>-1</sup>) for calibration source, (counts divided by count time (s))
- $R_b$  = count rate (s<sup>-1</sup>) for blank or background source, (counts divided by count time (s))
- $IF$  = correction factor for ingrowth of <sup>210</sup>Pb from <sup>210</sup>Pb between the time of the bismuth separation to the midpoint of counting,  $1 - e^{-\lambda_{Bi}(t_m - t_s)}$ , where:
  - $\lambda_{Bi}$  = decay constant for <sup>210</sup>Pb, (1.60 × 10<sup>-6</sup> s<sup>-1</sup>),
  - $t_s$  = date and time of <sup>210</sup>Pb separation, and
  - $t_m$  = midpoint of count of calibration mount (date and time).
- $DF$  = correction factor for decay of <sup>210</sup>Pb in the carrier solution from the carrier activity reference date to the time of the bismuth separation,  $e^{-\lambda_{Pb}(t_s - t_r)}$ , where:
  - $\lambda_{Pb}$  = decay constant for <sup>210</sup>Pb, (9.85 × 10<sup>-10</sup> s<sup>-1</sup>),
  - $t_r$  = reference date and time of <sup>210</sup>Pb calibration of lead carrier, and
  - $t_s$  = date and time of <sup>210</sup>Pb separation.
- $c_s$  = activity concentration (or massic activity) of the calibration standard solution (Bq/unit),
- $V_s$  = volume (or mass) of standard solution used (mL or g),
- $Y_{Pb}$  = chemical yield of lead (see Sections 13.1 and 13.2);  $Y_{Pb} = m_s / (c_c \times V_c)$ , where:
  - $m_s$  = net mass (mg) of lead sulfate found in the source, equal to  $m_{F+P} - m_F$ , where  $m_{F+P}$  is the total mass of the filter plus precipitate and  $m_F$  is the tare mass (filter only),
  - $c_c$  = mass concentration (mg/mL) of lead (as sulfate) in the carrier solution (see Eq 5), and
  - $V_c$  = volume of carrier solution added (mL).

Eq 1 assumes that any <sup>210</sup>Pb activity contamination in the Pb carrier is insignificant compared to the amount of <sup>210</sup>Pb activity in the calibration source spike.

11.1.8 The variance in the <sup>210</sup>Pb detector efficiency,  $\varepsilon_{Bi}$ , (not the average) is calculated by Eq 2:

$$u_c^2(\varepsilon_{Bi}) = \left( \frac{u^2(R_a) + u^2(R_b)}{m_s^2 \times IF^2} + \left( \frac{R_a - R_b}{m_s \times IF} \right)^2 \times \frac{u^2(m_s)}{m_s^2} + u^2(\hat{F}_c) \times DF_c^2 \right) \times \frac{c_c^2 \times V_c^2}{c_s^2 \times V_s^2 \times DF^2} + \varepsilon_{Bi}^2 \times \left( \frac{u^2(c_s)}{c_s^2} + \frac{u^2(V_s)}{V_s^2} + \frac{u^2(c_c)}{c_c^2} + \frac{u^2(V_c)}{V_c^2} \right) \quad (2)$$

where  $u(\cdot)$  denotes standard uncertainty; for example,  $u(V_s)$  is the standard uncertainty of  $V_s$ .

11.1.8.1 Eq 2 omits the uncertainties due to the activity concentration of the calibration standard solution,  $c_s$ , and the concentration of the carrier solution,  $c_c$ . These uncertainty components are accounted for when the average efficiency is determined (below).

11.1.8.2 The procedure requires an average of (at least) three efficiencies ( $N = 3$ ) measured using three calibration sources on each detector. For this purpose, calculate  $\varepsilon_1$ ,  $\varepsilon_2$ ,  $\varepsilon_3$  for each source, and use Eq 3 to calculate the weighted average:

$$\bar{\varepsilon}_{Bi} = \frac{1}{N} \sum_{i=1}^N \varepsilon_i \quad (3)$$

11.1.8.3 To calculate the uncertainty of the average, including uncertainty components due to systematic errors, Eq 4 is used:

$$u(\bar{\varepsilon}_{Bi}) = \sqrt{\frac{1}{N^2} \sum_{i=1}^N u_c^2(\varepsilon_i) + \bar{\varepsilon}_{Bi}^2 \times \left( \frac{u^2(c_s)}{c_s^2} + \frac{u^2(c_c)}{c_c^2} \right)} \quad (4)$$

### 11.2 Determination of Inherent <sup>210</sup>Pb in Pb Carrier:

11.2.1 As noted in Section 6.2, in cases where the Pb carrier used in this procedure has not been determined to be free of <sup>210</sup>Pb, the <sup>210</sup>Pb content inherent in the lead carrier used in this method must be evaluated. Each new carrier solution must be measured for <sup>210</sup>Pb prior to use. Once the <sup>210</sup>Pb content of the lead carrier is known, the <sup>210</sup>Pb count rate from the recovered lead carrier can be calculated for each sample analyzed. The following step provides a protocol to determine the inherent <sup>210</sup>Pb in the lead carrier and Section 13 provides the equations needed to correct for the <sup>210</sup>Pb inherent in the lead carrier. The specific number of samples, as well as acceptance criteria for the data and statistical tests to determine detectable <sup>210</sup>Pb in the lead carrier, should be specified in the laboratory's Quality Systems Manual.

11.2.2 To a minimum of five 50 mL centrifuge tubes, add 1 mL of the Pb carrier solution.

11.2.3 Add 20 mL of water and 4 mL concentrated sulfuric acid to each centrifuge tube.

11.2.4 Continue with the normal sample preparation, beginning at Section 12.16.

11.2.5 After counting, calculate for each sample the <sup>210</sup>Pb concentration and associated uncertainty according to Section 13. Calculate the weighted average  $\hat{a}_c$  and standard uncertainty  $u(\hat{a}_c)$  of the <sup>210</sup>Pb concentration using the calculated sample results from the data set using the equations in Section 13.3.

## 12. Procedure

NOTE 2—See Fig. 1 for a diagram of the procedure.

ASTM <sup>210</sup>Pb Method for Water Samples

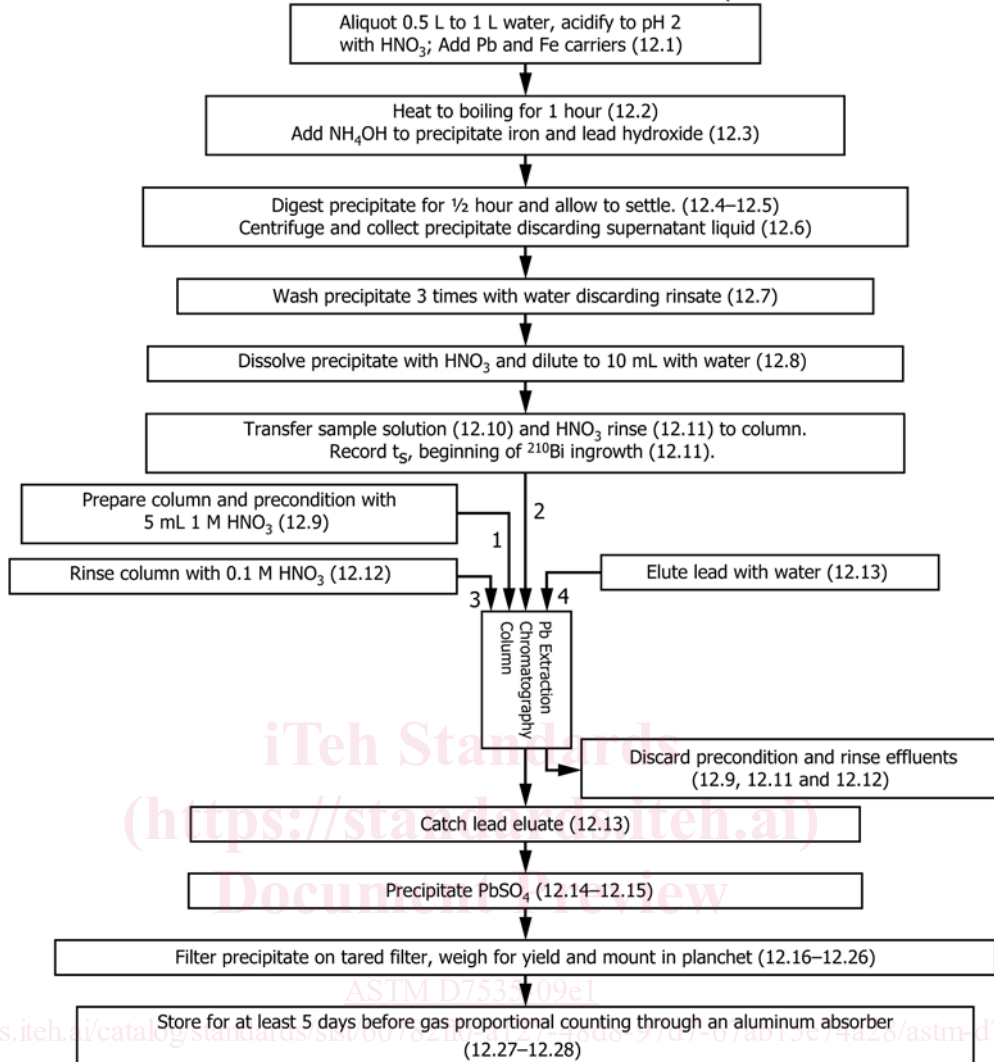


FIG. 1 <sup>210</sup>Pb Method for Water Samples

12.1 Add 1.0 mL of lead carrier and 1.0 mL of iron carrier to a maximum 500 mL of sample. Acidify sample with nitric acid to pH 2.

12.2 Cover beaker with a watch glass and heat at near boiling for an hour. Reduce heat.

12.3 Remove watch glass. Carefully, with stirring, add approximately 12 mL of concentrated ammonium hydroxide to precipitate iron hydroxide. Add more if necessary to form a precipitate.

12.4 Heat the sample without boiling for another 30 minutes.

12.5 Let the precipitate settle for at least 2 hours (preferably overnight). Decant the supernatant. Transfer the remaining sample along with the precipitate into a 50 mL plastic centrifuge tube.

12.6 Centrifuge at approximately 3500 RPM for approximately 15 minutes and discard the supernatant.

12.7 Wash the precipitate with 10 mL of water. Centrifuge and discard the supernatant. Repeat this step two more times to ensure removal of ammonia prior to the next step.

12.8 Dissolve residue in 1.2 mL of 8 M HNO<sub>3</sub>, then dilute to a final volume of 10 mL with water, bringing the final solution to a concentration of 1 M HNO<sub>3</sub>.

12.9 Prepare a lead extraction chromatography column by removing the bottom plug and the cap. Press the top frit down snugly to the resin surface using a glass rod (or equivalent) and let the water drain out. Add 5 mL of 1 M HNO<sub>3</sub> and allow the solution to drain by gravity.

12.10 Carefully transfer the sample solution to the reservoir of the column.

12.11 Rinse centrifuge tube with 10 mL of 1 M HNO<sub>3</sub> and add to the column after the feed has passed through. Record the time and date of this rinse. This will be the start of <sup>210</sup>Bi ingrowth, *t<sub>s</sub>*.