ILLINOIS POLLUTION CONTROL BOARD

PC #7

IN THE MATTER OF: WASTEWATER PRETREATMENT UPDATE, USEPA AMENDMENTS (January) 1, 2007 through June 30, 2007	)	**R08-5 (Identical-Substance Rulemaking-Pubic Water Supply**
SDWA UPDATE, USEPA AMENDMENTS (January 1, 2007 through June 30, 2007 and June 2, 2007)	)	**R08-7 (Identical-in-Substance Rulemaking-Public Water Supply**
SDWA UPDATE, USEPA AMENDMENTS (July 1, 2007 through December 31, 2007	)	**R08-13 (Identical-in-Substance Rulemaking-Public Water Supply**

NOTICE OF FILING

John Therriault, Clerk
Illinois Pollution Control Board
James R. Thompson Center
100 W. Randolph, Suite 11-500
Chicago, IL 60601

General Counsel
Illinois Dept. Of Natural Resources
One Natural Resources Way
Springfield, IL 62702-1271

Matt Dunn, Environmental Bureau Chief
Office of the Attorney General
69 West Washington Street, Suite 1800
Chicago, IL 60602

PLEASE TAKE NOTICE that I have filed with the Office of the Clerk of the Pollution Control Board the Illinois Environmental Protection Agency's Comments in the above captioned matter, a copy of which is herewith served upon you.

Date: November 7, 2008

ILLINOIS ENVIRONMENTAL PROTECTION AGENCY

By: Stefanie N. Diers

Stefanie N. Diers
Assistant Counsel
Division of Legal Counsel

1021 North Grand Avenue East
Springfield, Illinois 62794-9276
(217) 782-5544

THIS FILING IS SUBMITTED ON RECYCLED PAPER

ILLINOIS POLLUTION CONTROL BOARD

IN THE MATTER OF:	)	
WASTEWATER PRETREATMENT	)	**R08-5**
UPDATE, USEPA AMENDMENTS (January	)	**(Identical-Substance**
1, 2007 through June 30, 2007	)	**Rulemaking-Pubic Water**
	)	**Supply)**
	)	
SDWA UPDATE, USEPA AMENDMENTS	)	**R08-7**
(January 1, 2007 through June 30, 2007 and	)	**(Identical-in-Substance**
June 2, 2007)	)	**Rulemaking-Public Water**
	)	**Supply)**
	)	
	)	
SDWA UPDATE, USEPA AMENDMENTS	)	**R08-13**
(July 1, 2007 through December 31, 2007	)	**(Identical-in-Substance**
	)	**Rulemaking-Public Water**
	)	**Supply)**

ILLINOIS ENVIRONMENTAL PROTECTION AGENCY'S COMMENTS

Now comes the Illinois Environmental Protection Agency ("Illinois EPA" or "Agency") by and through its attorney and hereby submits the following comments in the above captioned cases. Illinois EPA respectfully states as follows:

COMMENTS WITH RESPEST TO THE BOARD'S ORDER AUGUST 7, 2008

1. Typo's occur on the following pages: 84(611.350), 90(611.351), 93(611.353), 97(611.354), 110(611.355), 129(611.356), 135(611.357), 139(611.358), 140(611.359a), 147(611.360) and 234(611.884). These are in the BOARD NOTE parts where (October 12, 2007) needs to be changed to (October 10, 2007).

2. There is a typo on Page 94 at 611.354 b) 1) ~~C~~3 - this needs to be changed to ~~3~~C .

3. Omission on Page 140 at 611.359(a)(2)(D) – second line, change to read "...described in subsection ~~(a)(2)~~ (a)(1) of this Section."

4. Typo on Page 194, Section 611.611(a)(18)(E), BOARD NOTE, next to last line: change "200" to "2000" .

5. Typo on Page 224, Section 611.720(a)(10)(B), BOARD NOTE, third line from top: "Method Method" change to a single "Method" .

6. Omission on Page235, Section 611.1004(b)(4), BOARD NOTE: last full line, change to read: "...Examination of Water and Wastewater, 20th edition, Method 9222D and G". **Reason for change:** This will be consistent with other citations to Standard Methods and the federal regulation.

COMMENTS WITH RESECT TO THE BOARD'S OPINION

7. On Page 11, in the header: "Revisions to the Lead and Copper Rule..." add 611.360 to the series of listings as this was omitted.

8. The following is in response to questions on Pages 10 and 11 of the Board Opinion.

A. Is there any reason the Board should include references to Standard Methods Online, where the same version of the Standard Method is available in the printed 21st edition of *Standard Methods*, considering that a Board note appended to the incorporation of *Standard Methods* cites to Standard Methods Online for purchase of individual methods?

Answer: The Agency has no objections to the Board proposal.

B. Can USEPA, the Agency, or anyone in the regulated community provide the Board with a copy of the method entitled "The Determination of Radium-226 and Radium-228 in Drinking Water by Gamma-ray Spectrometry Using HPGE or Ge(Li) Detectors," Revision 1.2, December 2004, cited by USEPA as available from the Environmental Resources Center at the Georgia Institute of Technology?

Answer: The Agency has obtained a copy of the Georgia Radium Method from US EPA Region V and is attaching a copy of that document with these comments.

C. Can USEPA, the Agency, or anyone in the regulated community provide the Board with a copy of Waters Method D6508, revision 2, entitled "Test Method for Determination of Dissolved Inorganic Anions in Aqueous Matrices Using Capillary Ion

Electrophoresis and Chromate Electrolyte," cited by USEPA as available from Waters Corporation?

Answer: The Agency received correspondence (attached) from Waters Corp. regarding Waters Method D6508 in which it is stated, the INSTRUMENT technology described therein (CE/CIA/CIE) is NO LONGER AVAILABLE from Waters, having been discontinued in mid-2001, and obsolete at the end of 2005. For those customers who operate an existing system, the Agency continues to offer some of the electrolyte solutions referred to in the method." Included with the note is a copy of ASTMD 6508 – 00 which the Agency takes to mean Waters Method 6508.

D. Can or should the Board substitute the easily located method ASTM D6508-00(2005)e2 in place of the Method cited as Waters Method D6508, revision 2 by USEPA, which the Board could not locate from the listed source?

Answer: Based on the correspondence noted in item C above, the Agency would have no objection to the Board adopting ASTM D6508-00(2005)e2 in light of the instrumentation being discontinued.

E. Did the Board take an acceptable approach to the approved equivalent methods, which USEPA codified as appendix A to 40 C.F.R. 141, by combining them with the methods that USEPA approved by rulemaking within the text of the regulations?

Answer: The Agency believes that the Board has taken the appropriate steps by incorporating the equivalent methods within the text of the regulations.

COMMENTS WITH RESPECT TO SECTION 611.355 (A-G)

9) With respect to the public education materials found in Section 611.355 (A-G), Illinois EPA respectfully disagrees with language proposed by the Board. The current procedures for reviewing and approving public education (PE) materials works effectively and has never been an issue for the many years the Agency has been

implementing the Lead and Copper Rule. The language proposed by the Board is not needed nor is it required to be included in the regulations.

The federal regulation rightly places the burden on the Community Water Supply ("CWS") to generate and distribute compliant PE materials. See 40 C.F.R. 141.85(a)(1) and (b)(2). When the Agency initially notifies the CWS that its lead action level has been exceeded, a comprehensive PE packet is sent which includes a self-assessment checklist of requirements, fill-in-the blank PE template(s), and a PE-preparation guidance document. The CWS prepares the PE, distributes the materials to the consumers and sends the Agency a copy along with completed forms attesting that the required PE requirements were met.

As soon as time and resources allow, the Agency reviews the PE information submitted, determines compliance, and issues a response to the CWS. Due to the amount of information initially provided to the CWS, the response most often indicates 100% compliance. If there are minor issues, then the CWS can correct these during any repeated notices. If there are major issues, the Agency would require re-issuance.

The language proposed by the Board is shifting the burden to the Agency and such a shift is unnecessary and burdensome. Therefore, the Agency respectfully request that the proposed language in Section 611.355(3)(A-G) be stricken in its entirety.

10) As stated above, the Agency would prefer that Section 611.355 (3)(A-G) be stricken. However, if that is unacceptable to the Board, the Agency offers the following suggestions with respect to the language proposed in 611.355(3)(A-G):

A) The supplier must submit all written public education materials to the Agency for review at least 60 days after the end of the sampling period.~~its planned date for delivery of the materials to the public.~~

By striking some of the language proposed by the Board it will allow the Agency a tracking method concerning the sampling periods.

B) If the Agency determines that the form and content of the supplier's written public education materials is adequate, it may issue a SEP pursuant to Section 611.110 that expressly approves the materials.

C) A supplier may immediately distribute its written public education materials after receipt of a SEP or a revised SEP that expressly approves those materials.

D) If the Agency determines that the form or content of the written public education materials submitted by the supplier does not comply with the requirements of this Sections, it must issue a SEP pursuant to Section 611.110. The Agency may issue a revised SEP that expressly supersedes a SEP previously issued under this subsection (a)(1). Any SEP or revised SEP issued by the Agency must identify any deficiencies in the written public education materials with specificity sufficient to guide the supplier to correct the deficiencies in a way that would address the Agency's concerns. The revised SEP shall be submitted to the Agency within 30 days after being notified of the deficiencies.

E) The Agency must issue any SEP or revised SEP under subsection (a)(3)(D) of this Section no later than 90 ~~30~~ days after the date on which it received a copy of the supplier's prospective written public education materials, unless the Agency and the supplier have agreed to a later date pursuant to subsection (a)(3)(F) of this Section. The Agency and the supplier may agree to a longer time within which the Agency may issue a SEP or a revised SEP, in which case the Agency must issue the SEP or revised SEP before expiration of the agreed upon extension ~~agreed longer time.~~

~~F) If the supplier has not received a SEP from the Agency within 45 days after the date on which the Agency received its written public education material, those materials are deemed approved, and the supplier may immediately distribute them.~~

The Agency respectfully disagrees with having the automatic approval process and proposes this paragraph be stricken altogether. This language is not needed based on the Agency's comments and such a requirement is not found in the federal regulations. Furthermore, the Agency is of the opinion that US EPA may not approve an automatic approval based on how they have developed precise content and delivery of the PE. Also, once a default approval is issued, the wrong information is in front of the public which could be contrary to the actions they should be taking. Trying to rescind the PE would only lead to more confusion, leading to a delay in getting the right information before the public while an enforcement case or law suit against the Agency is being processed.

However, should the Board determine that that 611.355 (A-G) is necessary and that an automatic approval is consistent with the federal rules, the Agency suggest a longer timeframe for Agency review before an automatic approval is granted.

G) Once the supplier has revised its written public education materials exactly as described by the Agency in a SEP issued under subsection (a)(3)(D) of this Section, those materials are deemed approved, and the supplier shall ~~may~~ immediately proceed to distribute them.

11) It should be noted that if the Board should determine that an automatic approval is **not** appropriate, the Agency suggest that that last sentence in 611.355(a)(1) should rewritten as follows:

> The supplier must submit all written public education materials prior to delivery. ~~as required by subsection (a)(3) of this Section.~~

12) The following is the Agency response to the Board request for comments on the numbered questions on Page 17 pertaining to Section 611.355(a)(1).

A. Is requiring written Agency action only where the Agency determines that deficiencies exist the best option for Agency review of the materials?

Answer: Requiring written action by the Agency only where the Agency finds deficiencies is not the best option to review the materials. The Agency believes that approval or deficiencies should be addressed in writing. Currently, this is how the Agency address this situations.

B. Is the provision that deems the materials approved and which allows the supplier to proceed and distribute the materials in the absence of an Agency response workable?

Answer: The Agency disagrees with the 45 day period set by the Board for approvals. This timeframe is burdensome on the Agency and does not recognize the uniqueness of every review. Also, the federal regulations do not require a 45 day review.

C. Do the times required for submission to the Agency and provided for Agency review work for the purpose?

Answer: The Agency is not sure the time line for submissions to the Agency and the review of work is doable based on our previous comment.

D. Does the provision that requires the Agency to describe the deficiencies it has found appear adequate and workable to assure that the supplier is given a clear indication of those deficiencies?

Answer: The Agency can describe the deficiencies to the suppliers.

E. Does the requirement that allows the supplier to proceed and distribute its materials after it has addressed the Agency-determined deficiencies appear adequate and workable to assure that the Agency concerns are addressed and that publication occurs as rapidly as possible?

Answer: The Agency agrees with the requirements that allows the supplier to proceed and distribute the materials after the Agency's concerns are addressed.

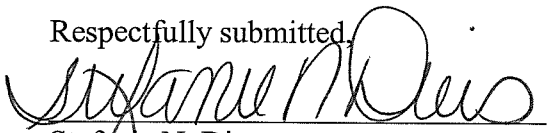
F. Is it necessary to set forth express provisions for Agency issuance of a revised SEP, and does such an express provision provide for the timeliest resolution of any issues that might arise in the course of Agency review of a supplier's public education materials?

Answer: The Agency is not sure how to address the issuance of a revised SEP. The process described by the Board seems confusing, so it would probably be best not to set forth express provision concerning the Agency's review. However, if the Board believes such language the Agency can issue a revised SEP but it is not clear what the timelines would be once a revision is required. The Agency suggestions that if a revision is required that the supplier make the necessary changes within 30 days.

COMMENTS WITH RESPECT TO THE BOARD'S SEPTEMBER 4, 2008 SUPPLEMETNAL OPINION AND ORDER

13) Illinois EPA notes that on Page 22 of the Board's Opinion the Board Note should be changed from 40 CFR 141.601(c) to 40 CFR 141.601(b).

Respectfully submitted,



Stefanie N. Diers
Assistant Counsel

Dated: November 7, 2008

1021 North Grand Avenue East
P.O. Box 19276
Springfield, Illinois 62794-9276
217-782-5544

ATTACHMENTS

Designation: D 6508 – 00 (Reapproved 2005)$^{\epsilon 1}$

Standard Test Method for Determination of Dissolved Inorganic Anions in Aqueous Matrices Using Capillary Ion Electrophoresis and Chromate Electrolyte[1]

This standard is issued under the fixed designation D 6508; 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 (ε) indicates an editorial change since the last revision or reapproval.

ϵ^1 NOTE—Warning notes were moved into the text in January 2005.

1. Scope

1.1 This test method cover the determination of the inorganic anions fluoride, bromide, chloride, nitrite, nitrate, ortho-phosphate, and sulfate in drinking water, wastewater, and other aqueous matrices using capillary ion electrophoresis (CIE) with indirect UV detection. See Figs. 1-6.

1.2 The test method uses a chromate-based electrolyte and indirect UV detection at 254 nm. It is applicable for the determination or inorganic anions in the range of 0.1 to 50 mg/L except for fluoride whose range is 0.1 to 25 mg/L.

1.3 It is the responsibility of the user to ensure the validity of this test method for other anion concentrations and untested aqueous matrices.

NOTE 1—The highest accepted anion concentration submitted for precision and bias extend the anion concentration range for the following anions: Chloride to 93 mg/L, Sulfate to 90 mg/L, Nitrate to 72 mg/L, and ortho-phosphate to 58 mg/L.

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 hazard statements, see Section 9.

2. Referenced Documents

2.1 *ASTM Standards:* [2]

D 1066 Practice for Sampling Steam
D 1129 Terminology Relating to Water
D 1193 Specification for Reagent Water
D 2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D 3370 Practices for Sampling Water from Closed Conduits
D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water
D 5810 Guide for Spiking into Aqueous Samples

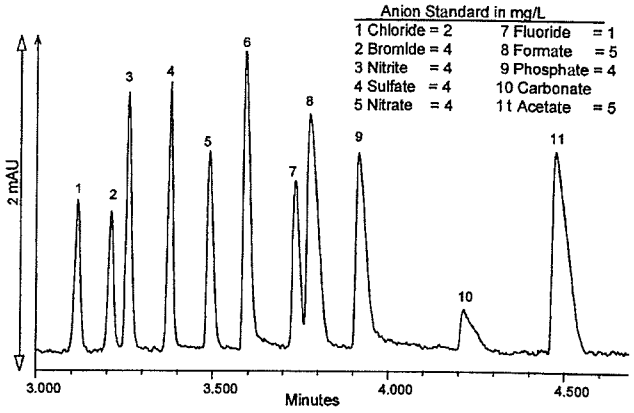


FIG. 1 Electropherogram of Mixed Anion Working Solution and Added Common Organic Acids

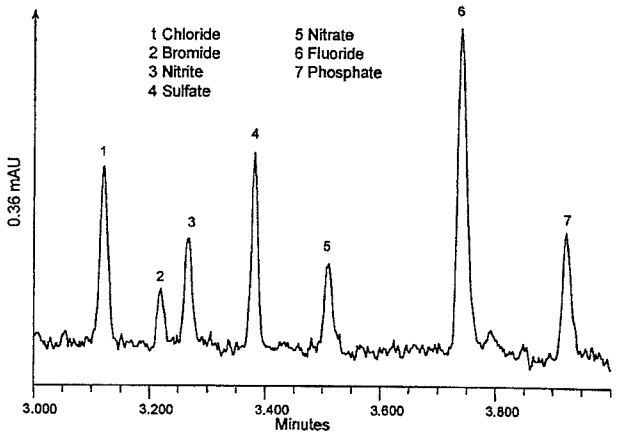


FIG. 2 Electropherogram of 0.2 mg/L Anions Used to Determine MDL

[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

Current edition approved Jan. 1, 2005. Published April 2005.

Originally approved in 2000. Last previous edition approved in 2000 as D 6508 – 00.

[2] 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.

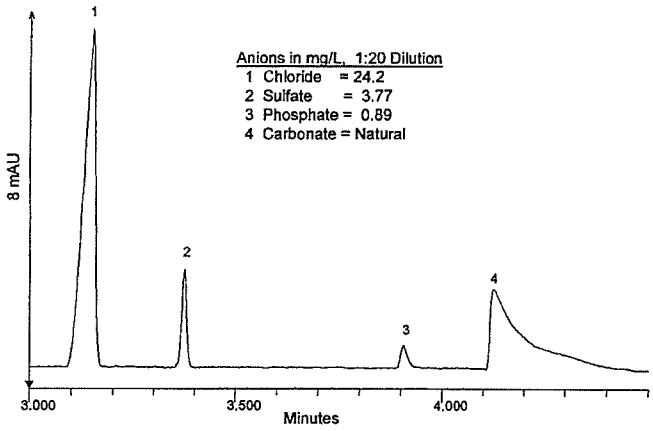


FIG. 3 Electropherogram of Substitute Wastewater

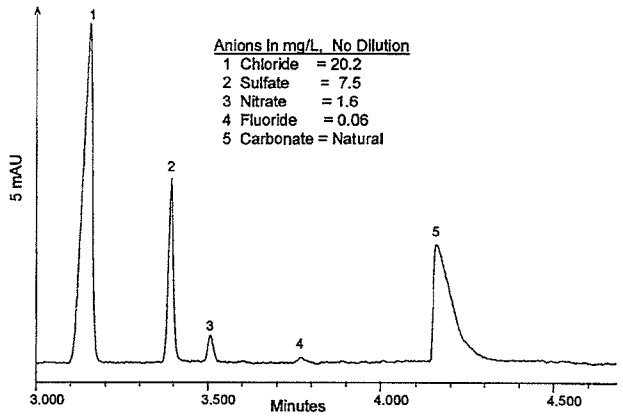


FIG. 4 Electropherogram of Drinking Water

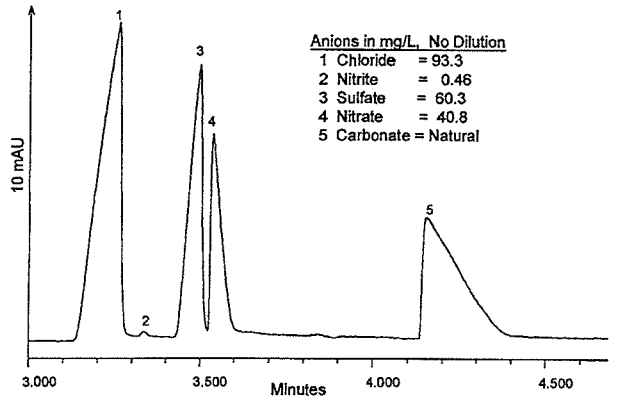


FIG. 5 Electropherogram of Municipal Wastewater Treatment Plant Discharge

D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

D 5905 Practice for the Preparation of Substitute Wastewater

F 488 Test Method for On-Site Screening of Heterotrophic Bacteria in Water

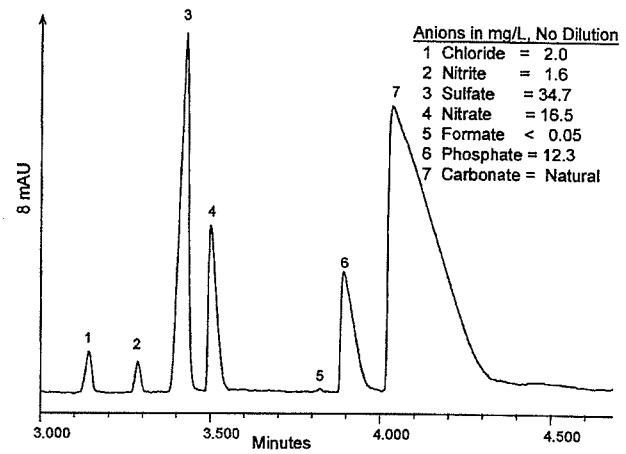


FIG. 6 Electropherogram of Industrial Wastewater

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *capillary ion electrophoresis, n*—an electrophoretic technique in which a UV-absorbing electrolyte is placed in a 50 μm to 75 μm fused silica capillary. Voltage is applied across the capillary causing electrolyte and anions to migrate towards the anode and through the capillary's UV detector window. Anions are separated based upon the their differential rates of migration in the electrical field. Anion detection and quantitation are based upon the principles of indirect UV detection.

3.2.2 *electrolyte, n*—a combination of a UV-absorbing salt and an electroosmotic flow modifier placed inside the capillary, used as a carrier for the analytes, and for detection and quantitation. The UV-absorbing portion of the salt must be anionic and have an electrophoretic mobility similar to the analyte anions of interest.

3.2.3 *electroosmotic flow (EOF), n*—the direction and velocity of electrolyte solution flow within the capillary under an applied electrical potential (voltage); the velocity and direction of flow is determined by electrolyte chemistry, capillary wall chemistry, and applied voltage.

3.2.4 *electroosmotic flow modifier (OFM), n*—a cationic quaternary amine in the electrolyte that dynamically coats the negatively charged silica wall giving it a net positive charge. This reverses the direction of the electrolyte's natural electroosmotic flow and directs it towards the anode and detector. This modifier augments anion migration and enhances speed of analysis. Its concentration secondarily effects anion selectivity and resolution, (see Fig. 7).

3.2.5 *electrophoretic mobility, n*—the specific velocity of a charged analyte in the electrolyte under specific electroosmotic flow conditions. The mobility of an analyte is directly related to the analyte's equivalent ionic conductance and applied voltage, and is the primary mechanism of separation.

3.2.6 *electropherogram, n*—a graphical presentation of UV-detector response versus time of analysis; the x axis is

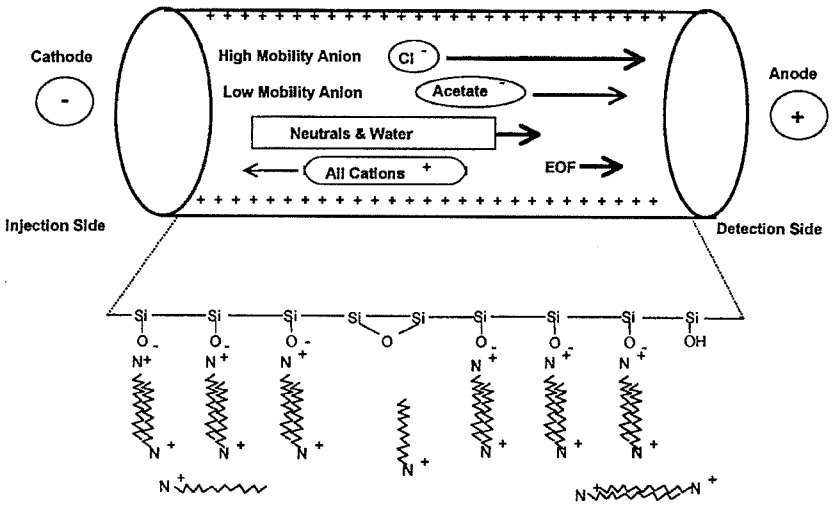


FIG. 7 Pictorial Diagram of Anion Mobility and ElectroOsomotic Flow Modifier

migration time, which is used to qualitatively identify the anion, and the y axis is UV response, which can be converted to time corrected peak area for quantitation.

3.2.7 *hydrostatic sampling, n*—a sample introduction technique in which the capillary with electrolyte is immersed in the sample, and both are elevated to a specific height, typically 10 cm, above the receiving electrolyte reservoir for a preset amount of time, typically less than 60 s. Nanolitres of sample are siphoned into the capillary by differential head pressure and gravity.

3.2.8 *indirect UV detection, n*—a form of UV detection in which the analyte displaces an equivalent net charge amount of the highly UV-absorbing component of the electrolyte causing a net decrease in background absorbance. The magnitude of the decreased absorbance is directly proportional to analyte concentration. Detector output polarity is reversed in order to obtain a positive mV response.

3.2.9 *midpoint of peak width, n*—CIE peaks typically are asymmetrical with the peak apex shifting with increasing concentration, and the peak apex may not be indicative of true analyte migration time. Midpoint of peak width is the midpoint between the analyte peak's start and stop integration, or the peak center of gravity.

3.2.10 *migration time, n*—the time required for a specific analyte to migrate through the capillary to the detector. The migration time in capillary ion electrophoresis is analogous to retention time in chromatography.

3.2.11 *time corrected peak area, n*—normalized peak area; peak area divided by migration time. CE principles state that peak area is dependent upon migration time, that is, for the same concentration of analyte, as migration time increases (decreases) peak area increases (decreases). Time corrected peak area accounts for these changes.

4. Summary of Test Method

4.1 Capillary ion electrophoresis, see Figs. 7-10, is a free zone electrophoretic technique optimized for the determination of anions with molecular weight less than 200. The anions migrate and are separated according to their mobility in the

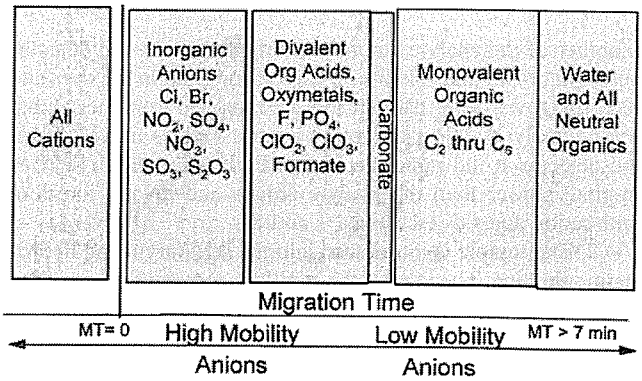


FIG. 8 Selectivity Diagram of Anion Mobility Using Capillary Ion Electrophoresis

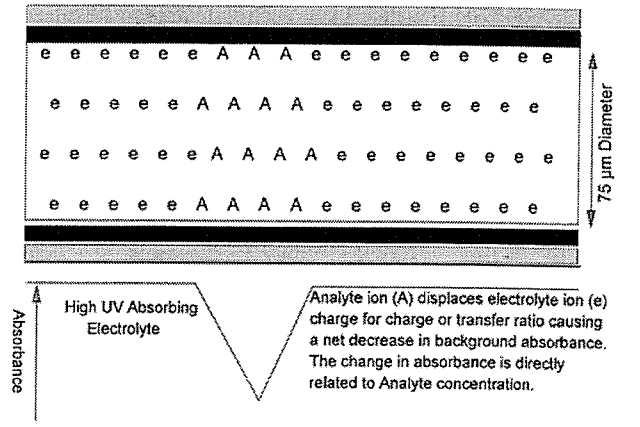


FIG. 9 Pictorial Diagram of Indirect UV Detection

electrolyte when an electrical field is applied through the open tubular fused silica capillary. The electrolyte's electroosmotic low modifier dynamically coats the inner wall of the capillary changing the surface to a net positive charge. This reversal of wall charge reverses the natural EOF. The modified EOF in combination with a negative power supply augments the

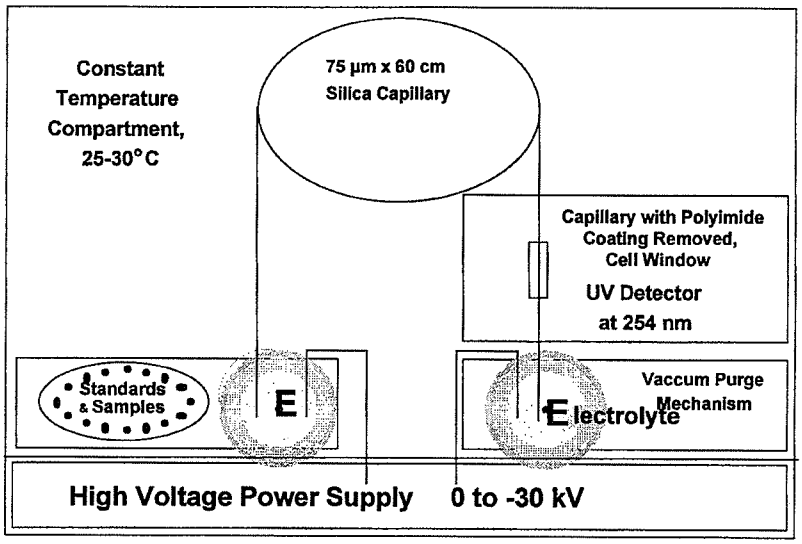


FIG. 10 General Hardware Schematic of a Capillary Ion Electrophoresis System

mobility of the analyte anions towards the anode and detector achieving rapid analysis times. Cations migrate in the opposite direction towards the cathode and are removed from the sample during analysis. Water and other neutral species move toward the detector at the same rate as the EOF. The neutral species migrate slower than the analyte anions and do not interfere with anion analysis (see Figs. 7 and 8).

4.2 The sample is introduced into the capillary using hydrostatic sampling. The inlet of the capillary containing electrolyte is immersed in the sample and the height of the sample raised 10 cm for 30 s where low nanolitre volumes are siphoned into the capillary. After sample loading, the capillary is immediately immersed back into the electrolyte. The voltage is applied initiating the separation process.

4.3 Anion detection is based upon the principles of indirect UV detection. The UV-absorbing electrolyte anion is displaced charge-for-charge by the separated analyte anion. The analyte anion zone has a net decrease in background absorbance. This decrease in UV absorbance in quantitatively proportional to analyte anion concentration (see Fig. 9). Detector output polarity is reversed to provide positive mV response to the data system, and to make the negative absorbance peaks appear positive.

4.4 The analysis is complete once the last anion of interest is detected. The capillary is vacuum purged automatically by the system of any remaining sample and replenished with fresh electrolyte. The system now is ready for the next analysis.

5. Significance and Use

5.1 Capillary ion electrophoresis provides a simultaneous separation and determination of several inorganic anions using nanolitres of sample in a single injection. All anions present in the sample matrix will be visualized yielding an anionic profile of the sample.

5.2 Analysis time is less than 5 minutes with sufficient sensitivity for drinking water and wastewater applications. Time between samplings is less than seven minutes allowing for high sample throughput.

5.3 Minimal sample preparation is necessary for drinking water and wastewater matrices. Typically, only a dilution with water is needed.

5.4 This test method is intended as an alternative to other multi-analyte methods and various wet chemistries for the determination of inorganic anions in water and wastewater. Compared to other multi-analyte methods the major benefits of CIE are speed of analysis, simplicity, and reduced reagent consumption and operating costs.

6. Interferences

6.1 Analyte identification, quantitation, and possible comigration occur when one anion is in significant excess to other anions in the sample matrix. For two adjacent peaks, reliable quantitation can be achieved when the concentration differential is less than 100:1. As the resolution between two anion peaks increase so does the tolerated concentration differential. In samples containing 1000 mg/L Cl, 1 mg/L SO_4 can be resolved and quantitated, however, the high Cl will interfere with Br and NO_2 quantitation.

6.2 Dissolved carbonate, detected as HCO_3^{-1}, is an anion present in all aqueous samples, especially alkaline samples. Carbonate concentrations greater than 500 mg/L will interfere with PO_4 quantitation.

6.3 Monovalent organic acids, except for formate, and neutral organics commonly found in wastewater migrate later in the electropherogram, after carbonate, and do not interfere. Formate, a common organic acid found in environmental samples, migrates shortly after fluoride but before phosphate. Formate concentrations greater than 5 mg/L will interfere with fluoride identification and quantitation. Inclusion of 2 mg/L formate into the mixed anion working solution aids in fluoride and formate identification and quantitation.

6.4 Divalent organic acids usually found in wastewater migrate after phosphate. At high concentrations, greater than 10 mg/L, they may interfere with phosphate identification and quantitation.

6.5 Chlorate also migrates after phosphate and at concentrations greater than 10 mg/L will interfere with phosphate identification and quantitation. Inclusion of 5 mg/L chlorate into the mixed anion working solution aids in phosphate and chlorate identification and quantitation.

6.6 As analyte concentration increases, analyte peak shape becomes asymmetrical. If adjacent analyte peaks are not baseline resolved, the data system will drop a perpendicular between them to the baseline. This causes a decrease in peak area for both analyte peaks and a low bias for analyte amounts. For optimal quantitation, insure that adjacent peaks are fully resolved, if they are not, dilute the sample 1:1 with water.

7. Apparatus

7.1 *Capillary Ion Electrophoresis System*—the system consists of the following components, as shown in Fig. 10 or equivalent:

7.1.1 *High Voltage Power Supply*, capable of generating voltage (potential) between 0 and minus 30 kV relative to ground with the capability working in a constant current mode.

7.1.2 *Covered Sample Carousel*, to prevent environmental contamination of the samples and electrolytes during a multi-sample batch analysis.

7.1.3 *Sample Introduction Mechanism*, capable of hydrostatic sampling technique, using gravity, positive pressure, or equivalent.

7.1.4 *Capillary Purge Mechanism*, to purge the capillary after every analysis with fresh electrolyte to eliminate any interference from the previous sample matrix, and to clean the capillary with other reagent, such as sodium hydroxide.

7.1.5 *UV Detector*, having the capability of monitoring 254 nm, or equivalent, with a time constant of 0.3 s.

7.1.6 *Fused Silica Capillary*—A 75 µm (inner diameter) x 375 µm (outer diameter) x 60 cm (length) having a polymer coating for flexibility, and noncoated section to act as the cell window for UV detection.[3]

7.1.7 *Constant Temperature Compartment*—To keep the samples, capillary, and electrolytes at constant temperature.

7.2 *Data System*—A computer system that can acquire data at 20 points/s minimum, express migration time in minutes to three decimal places, use midpoint of the analyte peak width, or center of gravity, to determine the analyte migration time, use normalized migration times with respect to a reference peak for qualitative identification, use time corrected peak area response for analyte quantitation, and express results in concentration units.[3]

NOTE 2—It is recommended that integrators or standard chromatographic data processing not be used with this test method.

7.3 *Anion Exchange Cartridges in the Hydroxide Form.*[3,4]

7.4 *Plastic Syringe*, 20-mL, disposable.

7.5 *Vacuum Filtration Apparatus*, capable for filtering 100 mL of reagent through a 0.45 µm aqueous filter.

8. Reagents and Materials

8.1 *Purity of Reagents*—Unless otherwise indicated, it is intended that all reagents shall conform to the reagent grade specification of the Analytical Reagents of the American Chemical Society, where such specifications are available.[5] Other grades may be used, provided it is first ascertained that the reagent is of sufficient high purity to permit its use without lessening the performance or accuracy of the determination. Reagent chemicals shall be used for all tests.

NOTE 3—Calibration and detection limits of this test method are biased by the purity of the reagents.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type I reagent water conforming or exceeding specification D 1193. Freshly drawn water should be used for preparation of all stock and working standards, electrolytes, and solutions.[6] Performance and detection limits of this test method are limited by the purity of reagent water, especially TOC.

8.3 *Reagent Blank*—Reagent water, or any other solution, used to preserve or dilute the sample.

8.4 *Individual Anion Solution, Stock*

NOTE 4—It is suggested that certified individual 1000 mg/L anion standards be purchased for use with this test method.

NOTE 5—All weights given are for anhydrous or dried salts. Reagent purity must be accounted for in order to calculate true value concentration. Certify against NIST traceable standards.

8.4.1 *Bromide Solution, Standard (1.0 mL = 1.00 mg Bromide)*—Dry approximately 0.5 g of sodium bromide (NaBr) for 6 h at 150°C and cool in a desiccator. Dissolve 0.128 g of the dry salt in a 100 mL volumetric flask with water, and fill to mark with water.

8.4.2 *Chloride Solution, Standard (1.0 mL = 1.00 mg Chloride)*—Dry approximately 0.5 g of sodium chloride (NaCl) for 1 h at 100°C and cool in a desiccator. Dissolve 0.165 g of the dry salt in a 100 mL a volumetric flask with water, and fill to mark with water.

8.4.3 *Fluoride Solution, Standard (1.0 mL = 1.00 mg Fluoride)*—Dry approximately 0.5 g of sodium fluoride (NaF) for 1 h at 100°C and cool in a desiccator. Dissolve 0.221 g of the dry salt in a 100 mL volumetric flask with water, and fill to mark with water.

8.4.4 *Formate Solution, Standard (1.0 mL = 1.00 mg Formate)*—Dissolve 0.151 g of sodium formate in a 100-mL volumetric flask with water, and fill to mark with water.

[3] The sole source of supply of the apparatus known to the committee at this time is Waters Corp., 34 Maple St., Milford, MA 01757. 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 [1], which you may attend.

[4] The sole source of supply of the apparatus known to the committee at this time is Alltech Associates, P/N 30254, 2051 Waukegan Rd., Deerfield, IL, 60015.

[5] *Reagent Chemicals, American Chemical Society Specifications*, Am. Chem. Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopoeia Convention, Inc. (USPC), Rockville, Md.

[6] Although the reagent water may exceed Specification D 1193, the reagent water needs to be periodically tested for bacterial contamination. Bacteria and their waste products may adversely affect system performance. As a guide, ASTM Type IA water specifies a total bacteria count of 10 colonies/L. Refer to Test Method F 488 for analysis procedure.

8.4.5 *Nitrate Solution, Standard (1.0 mL = 1.00 mg Nitrate)*—Dry approximately 0.5 g of sodium nitrate ($NaNO_3$) for 48 h at 105°C and cool in a desiccator. Dissolve 0.137 g of the dry salt in a 100-mL volumetric flask with water, and fill to mark with water.

8.4.6 *Nitrite Solution, Standard (1.0 mL = 1.00 mg Nitrite)*—Dry approximately 0.5 g of sodium nitrite ($NaNO_2$) for 24 h in a desiccator containing concentrated sulfuric acid. Dissolve 0.150 g of the dry salt in a 100-mL volumetric flask with water, and fill to mark with water. Store in a sterilized glass bottle. Refrigerate and prepare monthly.

NOTE 6—Nitrite is easily oxidized, especially in the presence of moisture. Use only fresh reagent.

NOTE 7—Prepare sterile bottles for storing nitrite solutions by heating for 1 h at 170°C in an air oven.

8.4.7 *Ortho-Phosphate Solution, Standard (1.0 mL = 1.00 mg o-Phosphate)*—Dissolve 0.150 g of anhydrous dibasic sodium phosphate (Na_2HPO_4) in a 100-mL volumetric flask with water, and fill to mark with water.

8.4.8 *Sulfate Solution, Standard (1.0 mL = 1.00 mg Sulfate)*—Dry approximately 0.5 g of anhydrous sodium sulfate (Na_2SO_4) for 1 h at 110°C and cool in a dessicator. Dissolve 0.148 g of the dry salt in a 100-mL volumetric flask with water, and fill to mark with water.

8.5 *Mixed Anion Solution, Working*—Prepare at least three different working standard concentrations for the analyte anions of interest bracketing the desired range of analysis, typically between 0.1 and 50 mg/L, and add 2 mg/L formate to all standards. Add an appropriate aliquot of Individual anion stock solution (see 8.4) to a prerinsed 100-mL volumetric flask, and dilute to 100 mL with water.

NOTE 8—Use 100 µL of Individual anion stock solution (see 8.4) per 100 mL for 1 mg/L anion.

NOTE 9—Anions of no interest may be omitted.

NOTE 10—The midrange mixed anion solution, working may be used for the determination of migration times and resolution described in 12.1.

8.6 *Calibration Verification Solution (CVS)*—A solution formulated by the laboratory of mixed analytes of known concentration prepared in water. The CVS solution must be prepared from a different source to the calibration standards.

8.7 *Performance Evaluation Solution (PES)*—A solution formulated by an independent source of mixed analytes of known concentration prepared in water. Ideally, the PES solution should be purchased from an independent source.

8.8 *Quality Control Solution (QCS)*—A solution of known analyte concentrations added to a synthetic sample matrix such as substitute wastewater that sufficiently challenges the test method.

8.9 *Buffer Solution (100 mM CHES/1 mM Calcium Gluconate)*—Dissolve 20.73 g of CHES (2-[N-Cyclohexylamino]-Ethane Sulfonic Acid) and 0.43 g of calcium gluconate in a 1-L volumetric flask with water, and dilute to 1 L with water. This concentrate may be stored in a capped glass or plastic container for up to one year.

8.10 *Chromate Concentrate Solution (100 mM Sodium Chromate)*—Dissolve 23.41 g of sodium chromate tetrahydrate ($Na_2CrO_4 \cdot 4\ H_2O$) in a 1-L volumetric flask with water, and dilute to 1 L with water. This concentrate may be stored in a capped glass or plastic container for up to one year.

8.11 *OFM Concentrate Solution (100 mM Tetradecyltrimethyl Ammonium Bromide)*—Dissolve 33.65 g of Tetradecyltrimethyl Ammonium Bromide (TTABr) in a 1-L volumetric flask with water, and dilute to 1 L with water. Store this solution in a capped glass or plastic container for up to one year.

NOTE 11—TTABr needs to be converted to the hydroxide form (TTAOH) for use with this test method. TTAOH is commercially available as 100 mM TTAOH, which is an equivalent substitute.

8.12 *Sodium Hydroxide Solution (500 mM Sodium Hydroxide)*—Dissolve 20 g of sodium hydroxide (NaOH) in a 1-L plastic volumetric flask with water, and dilute to 1 L with water.

8.13 *Electrolyte Solution, Working (4.7 mM Chromate/4 mM TTAOH/10 mM CHES/0.1 mM Calcium Gluconate)*[3,7]—Wash the anion exchange cartridge in the hydroxide form (see 7.3) using the 20-mL plastic syringe (see 7.4) with 10 mL of 500 mM NaOH (see 8.12) followed by 10 mL of water. Discard the washings. Slowly pass 4-mL of the 100 mM TTABr solution (see 8.11) through the cartridge into a 100-mL volumetric flask. Rinse the cartridge with 20 mL of water, adding the washing to the volumetric flask.

NOTE 12—The above procedure is used to convert the TTABr to TTAOH, which is used in the electrolyte. If using commercially available 100 mM TTAOH, the above conversion step is not necessary; substitute 4 mL of 100 mM TTAOH and continue below.

8.13.1 Into the 100-mL volumetric flask add 4.7 mL of chromate concentrate solution (see 8.10) and 10 mL of buffer solution (see 8.9). Mix and dilute to 100 mL with water. The natural pH of the electrolyte should be 9 ± 0.1. Filter and degas using the vacuum filtration apparatus. Store the any remaining electrolyte in a capped glass or plastic container at ambient temperature. The electrolyte is stable for one year.

9. Precautions

9.1 Chemicals used in this test method are typical of many useful laboratory chemicals, reagents, and cleaning solutions, which can be hazardous if not handled properly. Refer to Guide D 3856.

9.2 It is the responsibility of the user to prepare, handle, and dispose of chemical solutions in accordance with all applicable federal, state, and local regulations. (**Warning**—This capillary electrophoresis method uses high voltage as a means for separating the analyte anions, and can be hazardous if not used properly. Use only those instruments that have all proper safety features.)

10. Sampling

10.1 Collect samples in accordance with Practice D 3370.

10.2 Rinse sample containers with sample and discard to eliminate any contamination from the container. Fill to overflowing and cap to exclude air.

[7] The sole source of supply of the apparatus known to the committee at this time is Waters Corp., 34 Maple St., Milford, MA 01757, as IonSelect High MobilityAnion Electrolyte, P/N 49385..

10.3 Analyze samples, as soon as possible, after collection. For nitrite, nitrate, and phosphate refrigerate the sample at 4°C after collection. Warm to room temperature before dilution and analysis.

10.4 At the laboratory, filter samples containing suspended solids through a prerinsed 0.45 µm aqueous compatible membrane filter before analysis.

10.5 If sample dilution is required to remain within the scope of this test method, dilute with water only.

11. Preparation of Apparatus

11.1 Set up the CE and data system according to the manufacturer's instructions.

11.2 Program the CE system to maintain a constant temperature of 25 ± 0.5°C, or 5°C above ambient laboratory temperature. Fill the electrolyte reservoirs with fresh chromate electrolyte working solution (see 8.13), and allow 10 minutes for thermal equilibration.

11.3 Condition a new capability (see 7.1.6) with 500 mM NaOH solution (see 8.12) for 5 minutes followed by water for 5 minutes. Purge the capillary with electrolyte (see 8.13) for 3 minutes.

11.4 Apply 15 kV of voltage and test for current. The current should be 14 ± 1 µA. If no current is observed, then there is a bubble, or blockage, or both, in the capillary. Degas the chromate electrolyte working solution and retry. If still no current, replace the capillary.

11.5 Set the UV detector to 254 nm detection, or equivalent. Zero the detector to 0.000 absorbance. UV offset is less than 0.1 AU.

11.6 Program the CE system for constant current of 14 µA.

11.7 Program the CE system for a hydrostatic sampling of 30 s. Approximately 37 nL of sample is siphoned into the capillary. Different sampling times may be used provided that the samples and standards are analyzed identically.

11.8 Program the CE system for 1 minute purge with the chromate electrolyte working solution between each analysis. Using a 15 psi vacuum purge mechanism, one 60-cm capillary volume can be displaced in 30 s.

11.9 Program the data system for an acquisition rate of at least 20 points/s. Program the data system to identify analyte peaks based upon normalized migration time using Cl as the reference peak, and to quantitate analyte peak response using time corrected peak area.

NOTE 13—Under the analysis conditions Cl is always the first peak in the electropherogram, and can be used as migration time reference peak.

12. Calibration

12.1 *Determination of Migration Times (Calibrate Daily)*—The migration time of an anion is dependent upon the electrolyte composition, pH, capillary surface and length, applied voltage, the ionic strength of the sample, and temperature. For every fresh electrolyte determine the analyte migration time, in min to the third decimal place, of the midrange mixed anion standard working solution (see 8.5), described in Section 11. Use the midpoint of analyte peak width as the determinant of analyte migration time.

NOTE 14—Analyte peak apex may be used as the migration time determinant, but potential analyte misidentification may result with asymmetrical peak shape at high analyte concentrations.

12.2 Analyze the blank (see 8.3) and at least three working mg/L solutions (see 8.5), using the set-up described in Section 11. For each anion concentration (X-axis) plot time corrected peak area response (Y-axis). Determine the best linear calibration line through the data points, or use the linear regression calibration routine (linear through zero) available in the data system.

NOTE 15—Do not use peak height for calibration. Peak area is directly related to migration time, that is, for the same analyte concentration, increasing migration time give increasing peak area.

12.2.1 The r^2 (coefficient of determination) values should be greater than 0.995; typical r^2 values obtained from the interlaboratory collaborative are given in Table A2.1.

12.3 Calibrate daily and with each change in electrolyte, and validate by analyzing the CVS solution (see 8.6) according to procedure in 16.4.

12.4 After validation of linear multiple point calibration, a single point calibration solution can be used between 0.1 and 50 mg/L for recalibration provided the quality control requirements in 16.4 are met.

13. Procedure

13.1 Dilute the sample, if necessary with water, to remain within the scope (see 1.2 and 1.3) and calibration of this test method. Refer to A1.5.1.

13.2 Analyze all blanks (see 8.3), standards (see 8.5), and samples as described in Section 11 using the quality control criteria described in 16.5-16.9. Refer to Figs. 1-6 for representative anion standard, detection limit standard, substitute wastewater, drinking water, and wastewater electropherograms.

13.3 Analyze all blanks, calibration standards, samples, and quality control solutions in singlicate.

13.3.1 *Optional*—Duplicate analyses are preferred due to short analysis times.

NOTE 16—Collaborative data was acquired, submitted and evaluated as the average of duplicate samplings.

13.4 After 20 sample analyses, or batch, analyze the QCS solution (see 8.8) If necessary, recalibrate using a single mixed anion standard working solution (see 8.5), and replace analyte migration time.

NOTE 17—A change in analyte migration time of the mixed anion standard working solution by more than +5% suggests that components in the previously analyzed sample matrices have contaminated the capillary surface. Continue but wash the capillary with NaOH solution (see 8.12) before the next change in electrolyte.

14. Calculation

14.1 Relate the time corrected peak area response for each analyte with the calibration curve generated in 12.2 to determine mg/L concentration of analyte anion. If the sample was diluted prior to analysis, then multiply mg/L anion by the dilution factor to obtain the original sample concentration, as follows:

$$\text{Original Sample mg/L Analyte} = (A \times SF) \quad (1)$$

where:
A = analyte concentration determined from the calibration curve, in mg/L, and
SF = scale or dilution factor.

15. Report Format

15.1 The sample analysis report should contain the sample name, analyte anion name, migration time reported to three decimal places, migration time ratio, peak area, time corrected peak area, sample dilution, and original solution analyte concentration.

15.1.1 *Optional*—Report analysis method parameters, date of sample data acquisition, and date of result processing for documentation and validation purposes.

16. Quality Control

16.1 Before this test method is applied to the analysis of unknown samples, the analyst should establish control according to procedures recommended in Practice D 5847, and Guide D 5810.

16.2 The laboratory using this test should perform an initial demonstration of laboratory capability according to procedures outlines in Practice D 5847.

NOTE 18—Certified performance evaluation solutions (PES) and QC solutions (QCS and CVS) are commercially available and recommended.

16.3 *Initial Demonstration of Performance*—Analyze seven replicates of a performance evaluation solution (PES) (see 8.7). The analyte concentration mean and standard deviation of the seven replicates should be calculated and compared to the test methods single operator precision for equivalent concentrations in reagent water given in Section 17.

16.3.1 Repeat the seven replicate analysis protocol before using a freshly prepared QVS solution (see 8.6) and QCS solution (see 8.8) for the first time. Calculate the standard deviation and compare with previous results using the student *t*-test. If no significant difference is noted, then use the combined standard deviation to determine the QC limits, generally the mean ± three standard deviations, for the QCV and QCS solutions.

16.4 *Calibration Verification*—After calibration, verify the calibration linearity and acceptable instrument performance using a calibration verification solution (see 8.6) treated as an unknown. If the determined CVS concentrations (see 8.6) are not within ± 3 standard deviations of the known true values as described in 16.3.1, the calibration solutions may be out of control. Reanalyze, and if analyte concentration still falls outside the acceptable limits, fresh calibration solutions (see 8.5) are required. Successful CVS analyte concentration must be confirmed after recalibration before continuing with the test method.

16.5 Analyze a reagent blank (see 8.3) with each batch to check for contamination introduced by the laboratory or use of the test method.

16.6 *Quality Control Solution*—Analyze one QCS (see 8.8) after 20 samples, or batch. The analyte concentrations for the QCS should fall within ± 3 standard deviations of historical values for the equivalent concentration and matrix. They are determined as described in 16.3.1.

Upper Control Limit = Analyte Mean Value + 3 times the Standard Deviation
Lower Control Limit = Analyte Mean Value – 3 times the Standard Deviation

16.7 *Matrix Spike Recovery*—One matrix spike (MS) should be analyzed with each batch of samples to test method recovery. Spike a portion of one sample from each batch with a known concentration of analyte, prepared in accordance with Guide D 3856. The % recovery of the spike should fall within %recovery ± analyst %RSD for an equivalent spike concentration and matrix given in Tables 1-7. If it does not, an interference may be present and the data for the set of similar samples matrices must be qualified with a warning that the data are suspect, or an alternate test method should be used. Refer to Guide D 5810.

16.7.1 If the known analyte concentration is between 15 and 50 mg/L, then spike the sample solution to increase analyte concentration by 50 %.

16.7.2 If the known analyte concentration is less than 15 mg/L, then spike the sample solution to increase analyte concentration by 100 %, but not less than 2 mg/L.

16.7.3 Calculate the percent recovery of the spike using the following formula:

$$\% \text{ Recovery} = 100\,[A\,(V_s + V) - B\,V_s]/C\,V \quad (2)$$

where:
A = Analyte concentration (mg/L) in spiked sample,
B = Analyte concentration (mg/L) in unspiked sample,
C = Concentration (mg/L) of analyte in spiking solution,
V_s = Volume (mL) of sample used, and
V = Volume (mL) added with spike,

Evaluate the performance according to Practice D 5847.

16.8 *Method Precision*—One unknown sample should be analyzed in triplicate with each batch to test method precision. Calculate the standard deviation and use the *F*-test to compare with the single operator precision give in Tables 1-7 for the equivalent analyte concentration and matrix type. Evaluate performance according to Practice D 5847.

16.9 The laboratory may perform additional quality control as desired or appropriate.

17. Precision and Bias

17.1 The precision and bias data presented in this test method meet the requirements of Practice D 2777, and are given in Tables 1-7.

17.2 This test method interlaboratory collaborative was performed by 11 laboratories using one operator each. Four Youden-Pair spike concentrations for the seven analytes anions yielding eight analyte concentration levels. Test data was submitted for eleven reagent waters, eleven substitute wastewaters, 15 drinking waters, and 13 wastewater sample matrices.

17.3 The precision, bias, and matrix recovery of this test method per anion analyte in four tested sample matrices are based upon the analyte true value, calculated using weight, volume, and purity. True value spiking solution concentrations are given in Table A1.4.

17.4 The bias and matrix recovery statements for less than 2 mg/L of chloride, sulfate, and nitrate in naturally occurring sample matrices may be misleading due to spiking of small analyte concentration into a high naturally occurring analyte

TABLE 1 Precision, Bias, and Matrix Recovery for Chloride

Matrix	No. of Values	True Value	Mean Result	Bias Versus True Value	Recovery Versus True Value	Interlab Std Dev *S(t)*	Interlab %RSD	Single Operator Std Dev. *S(o)*	Analyst %RSD
Reagent water	9	0.50	0.55	0.05	110.0	0.11	19.8		
	10	0.71	0.69	–0.02	97.2	0.08	11.5	0.05	7.5
	10	2.00	1.97	–0.03	98.5	0.14	6.8		
	9	2.98	2.97	–0.01	99.7	0.11	3.8	0.05	2.1
	10	14.92	14.76	–0.16	98.9	0.61	4.2		
	10	19.91	19.81	–0.10	99.5	0.81	4.1	0.48	2.8
	10	39.81	38.58	–1.23	96.9	1.43	3.7		
	10	49.76	48.70	–1.06	97.9	1.94	4.0	1.36	3.1
Substitute wastewater	9	0.50	0.46	–0.04	92.0	0.51	111.1		
	9	0.71	0.43	–0.28	60.6	0.69	160.7	0.42	93.8
	9	2.00	1.52	–0.48	76.0	0.68	45.0		
	9	2.98	2.58	–0.40	86.6	0.63	24.5	0.50	24.3
	9	14.92	14.29	–0.63	95.8	1.02	7.1		
	9	19.91	18.93	–0.98	95.1	1.24	6.6	0.60	3.6
	9	39.81	37.34	–2.47	93.8	5.44	14.6		
	9	49.76	47.54	–2.22	95.5	3.13	6.6	4.43	10.4
Drinking water	12	0.50	0.63	0.13	126.0	0.67	106.1		
	12	0.71	0.75	0.04	105.6	0.34	45.5	0.40	57.2
	12	2.00	2.15	0.15	107.5	0.51	23.6		
	12	2.98	2.95	–0.03	99.0	0.39	13.1	0.47	18.5
	12	14.92	14.54	–0.38	97.5	0.71	4.9		
	12	19.91	19.09	–0.82	95.9	1.11	5.8	0.37	2.2
	12	39.81	38.38	–1.43	96.4	1.56	4.1		
	12	49.76	47.97	–1.79	96.4	2.19	4.6	1.26	3.9
"Real" Wastewater	9	0.50	0.42	–0.08	84.0	0.34	81.0		
	10	0.71	0.47	–0.24	66.2	0.34	72.6	0.26	59.3
	10	2.00	1.56	–0.44	78.0	0.51	32.7		
	9	2.98	2.78	–0.20	93.3	0.19	6.8	0.37	17.3
	10	14.92	14.29	–0.63	95.8	0.63	4.4		
	10	19.91	18.83	–1.08	94.6	0.78	4.1	0.46	2.8
	9	39.81	37.01	–2.80	93.0	2.78	7.5		
	10	49.76	48.24	–1.52	96.9	3.15	6.5	2.54	6.0

concentration observed with the matrix blank. The commonly occurring analyte concentrations observed in the sample matrix blanks for the naturally occurring tested matrices are given in Table A1.5.

17.5 The high nitrate bias and %recovery noted for the 0.5 mg/L NO_3 spike solution are attributed to the spiking solution containing 50 mg/L nitrite and 0.5 mg/L nitrate. Refer to Annex Table A1.4, Solution 3. Some of the nitrite converted to nitrate prior to analysis. Similar NO_x conversion effect is observed with the 2-mg/L nitrate and 2 mg/L nitrite spike, Solution 7.

17.6 All collaborative participants used the premade chromate electrolyte.[7] Ten laboratories used a Waters CIA Analyzer with Millennium Data Processing Software, and one laboratory used a Agilent CE System with Diode Array Detector that provided equivalent results.

NOTE 19—Refer to reference B1.16 and Agilent (the former HP company) website for recommended operating conditions.

18. Keywords

18.1 anion; capillary electrophoresis; drinking water; ion analysis; reagent water; substitute wastewater; wastewater

TABLE 2 Precision, Bias, and Matrix Recovery for Bromide

Matrix	No. of Values	True Value	Mean Result	Bias Versus True Value	Recovery Versus True Value	Interlab Std Dev *S(t)*	Interlab %RSD	Single Operator Std Dev. *S(o)*	Analyst %RSD
Reagent water	10	0.51	0.60	0.09	117.6	0.19	31.0		
	10	0.70	0.83	0.13	118.6	0.23	28.2	0.10	14.6
	10	2.00	2.06	0.06	103.0	0.14	6.6		
	10	3.01	2.88	−0.13	95.7	0.23	7.9	0.15	6.3
	10	14.93	15.00	0.07	100.5	0.58	3.9		
	10	19.91	19.32	−0.59	97.0	0.97	5.0	0.75	4.4
	10	39.81	39.66	−0.15	99.6	1.24	3.1		
	10	49.77	50.04	0.27	100.5	2.94	5.9	1.61	3.6
Substitute wastewater	9	0.51	0.67	0.16	131.4	0.19	28.8		
	9	0.70	0.96	0.26	137.1	0.21	21.8	0.08	9.3
	9	2.00	2.14	0.14	107.0	0.22	10.2		
	9	3.01	2.72	−0.29	90.4	0.35	12.8	0.17	7.0
	9	14.93	14.70	−0.23	98.5	0.58	3.9		
	9	19.91	18.91	−1.00	95.0	2.62	13.8	1.63	9.7
	9	39.81	38.76	−1.05	97.4	1.11	2.9		
	9	49.77	48.81	−0.96	98.1	1.52	3.1	0.48	1.1
Drinking water	13	0.51	0.58	0.07	113.7	0.25	43.4		
	13	0.70	0.83	0.13	118.6	0.22	26.5	0.14	19.9
	13	2.00	1.98	−0.02	99.0	0.25	12.5		
	13	3.01	2.56	−0.45	85.0	0.25	9.7	0.15	6.8
	13	14.93	14.63	−0.30	98.0	0.50	3.4		
	13	19.91	19.22	−0.69	96.5	1.10	5.7	0.77	4.6
	13	39.81	38.97	−0.84	97.9	1.99	5.1		
	13	49.77	48.74	−1.03	97.9	1.49	3.1	1.13	2.6
"Real" Wastewater	11	0.51	0.59	0.08	115.7	0.11	19.3		
	12	0.70	0.78	0.08	111.4	0.19	24.4	0.10	14.0
	11	2.00	2.08	0.08	104.0	0.13	6.3		
	12	3.01	2.70	−0.31	89.7	0.41	15.1	0.27	11.5
	12	14.93	15.16	0.23	101.5	0.90	6.0		
	11	19.91	19.46	−0.45	97.7	1.63	8.4	1.09	6.3
	12	39.81	40.24	0.43	101.1	2.27	5.7		
	12	49.77	49.97	0.20	100.4	2.52	5.0	0.91	2.0

TABLE 3 Precision, Bias, and Matrix Recovery for Nitrite

Matrix	No. of Values	True Value	Mean Result	Bias Versus True Value	Recovery Versus True Value	Interlab Std Dev *S(t)*	Interlab %RSD	Single Operator Std Dev. *S(o)*	Analyst %RSD
Reagent water	9	0.50	0.62	0.12	124.0	0.16	26.1		
	9	0.70	0.72	0.02	102.9	0.08	10.5	0.05	7.1
	10	2.00	1.31	–0.69	65.5	0.25	19.2		
	10	2.98	3.11	0.13	104.4	0.17	5.4	0.13	6.0
	10	14.86	14.70	–0.16	98.9	0.47	3.2		
	10	19.81	19.88	0.07	100.4	0.70	3.5	0.27	1.5
	10	39.61	39.90	0.29	100.7	0.88	2.2		
	10	49.52	48.24	–1.28	97.4	1.34	2.8	1.25	2.8
Substitute wastewater	9	0.50	0.37	–0.13	74.0	0.22	59.7		
	9	0.70	0.59	–0.11	84.3	0.28	48.1	0.21	43.2
	10	2.00	1.25	–0.75	62.5	0.38	30.8		
	9	2.98	2.62	–0.36	87.9	0.82	31.4	0.43	22.1
	9	14.86	14.40	–0.46	96.9	0.58	4.0		
	10	19.81	19.50	–0.31	98.4	1.66	8.5	0.81	4.8
	10	39.61	39.97	0.36	100.9	2.02	5.0		
	9	49.52	49.09	–0.43	99.1	3.03	6.2	2.11	4.7
Drinking water	11	0.50	0.52	0.02	104.0	0.08	14.4		
	12	0.70	0.74	0.04	105.7	0.17	23.3	0.09	13.5
	12	2.00	1.30	–0.70	65.0	0.21	15.9		
	12	2.98	2.97	–0.01	99.7	0.14	4.6	0.16	7.4
	11	14.86	14.60	–0.26	98.3	0.40	2.8		
	11	19.81	19.82	0.01	100.1	0.59	3.0	0.26	1.5
	11	39.61	39.35	–0.26	99.3	0.99	2.5		
	12	49.52	49.14	–0.38	99.2	1.93	3.9	0.64	1.5
"Real" Wastewater	9	0.50	0.55	0.05	110.0	0.13	24.5		
	10	0.70	0.73	0.03	104.3	0.24	32.9	0.07	10.8
	9	2.00	1.27	–0.73	63.5	0.18	14.2		
	10	2.98	2.99	0.01	100.3	0.19	6.2	0.15	7.0
	10	14.86	14.55	–0.31	97.9	0.46	3.1		
	10	19.81	19.68	–0.13	99.3	0.71	3.6	0.38	2.2
	9	39.61	39.21	–0.40	99.0	1.03	2.6		
	9	49.52	47.27	–2.25	95.5	3.50	7.4	2.40	5.6

TABLE 4 Precision, Bias, and Matrix Recovery for Sulfate

Matrix	No. of Values	True Value	Mean Result	Bias Versus True Value	Recovery Versus True Value	Interlab Std Dev *S(t)*	Interlab %RSD	Single Operator Std Dev. *S(o)*	Analyst %RSD
Reagent water	9	0.49	0.49	0.00	100.0	0.18	37.5		
	10	0.70	0.71	0.01	101.4	0.20	29.2	0.05	8.3
	10	1.98	2.04	0.06	103.0	0.19	9.7		
	10	2.98	3.09	0.11	103.7	0.24	7.9	0.06	2.5
	10	14.86	14.67	–0.19	98.7	0.57	4.0		
	10	19.81	19.67	–0.14	99.3	0.73	3.8	0.44	2.6
	10	39.60	39.66	0.06	100.2	0.92	2.4		
	10	49.51	49.27	–0.24	99.5	1.26	2.6	0.49	1.1
Substitute wastewater	9	0.49	0.38	–0.11	77.6	0.25	66.9		
	9	0.70	0.51	–0.19	72.9	0.08	16.4	0.18	39.3
	9	1.98	1.83	–0.15	92.4	0.29	16.2		
	9	2.98	2.86	–0.12	96.0	0.31	11.2	0.20	8.6
	9	14.86	14.19	–0.67	95.5	1.06	7.7		
	9	19.81	19.23	–0.58	97.1	0.97	5.2	0.46	2.8
	9	39.60	38.45	–1.15	97.1	1.33	3.6		
	9	49.51	47.75	–1.76	96.4	1.43	3.1	0.75	1.8
Drinking water	12	0.49	0.41	–0.08	83.7	0.21	52.8		
	12	0.70	0.41	–0.29	58.6	0.20	50.3	0.14	34.3
	13	1.98	1.77	–0.21	89.4	0.53	30.3		
	13	2.98	2.68	–0.30	89.9	0.42	16.2	0.27	12.1
	13	14.86	14.25	–0.61	95.9	1.11	8.0		
	12	19.81	19.31	–0.50	97.5	1.39	7.4	1.48	8.9
	12	39.60	38.58	–1.02	97.4	1.96	5.2		
	13	49.51	48.43	–1.08	97.8	2.04	4.3	1.44	3.3
"Real" Wastewater	10	0.49	0.37	–0.12	75.5	0.39	106.4		
	11	0.70	0.16	–0.54	22.9	1.19	765.2	0.47	179.6
	11	1.98	1.57	–0.41	79.3	0.87	55.4		
	11	2.98	2.53	–0.45	84.9	0.64	25.4	0.24	11.9
	11	14.86	14.69	–0.17	98.9	1.26	8.6		
	10	19.81	19.38	–0.43	97.8	0.90	4.6	0.57	3.4
	11	39.60	38.74	–0.86	97.8	1.71	4.4		
	10	49.51	48.36	–1.15	97.7	1.51	3.1	0.47	1.1

TABLE 5 Precision, Bias, and Matrix Recovery for Nitrate

Matrix	No. of Values	True Value	Mean Result	Bias Versus True Value	Recovery Versus True Value	Interlab Std Dev *S(t)*	Interlab %RSD	Single Operator Std Dev. *S(o)*	Analyst %RSD
Reagent water	10	0.50	1.02	0.52	204.00	0.08	7.4		
	10	0.69	0.71	0.02	102.90	0.08	11.6	0.06	6.4
	11	1.99	2.83	0.84	142.21	0.23	8.1		
	11	2.97	2.89	–0.08	97.31	0.18	6.4	0.14	5.0
	11	14.91	14.77	–0.14	99.06	0.44	3.0		
	11	19.18	19.77	0.59	103.08	0.64	3.2	0.24	1.4
	10	39.86	39.09	–0.77	98.07	1.43	3.7		
	10	49.77	48.93	–0.84	98.31	1.72	3.5	0.62	1.4
Substitute wastewater	11	0.50	1.18	0.68	236.00	0.41	34.9		
	10	0.69	0.55	–0.14	79.71	0.30	55.3	0.42	4.9
	10	1.99	2.70	0.71	135.68	0.42	15.4		
	10	2.97	2.33	–0.64	78.45	1.10	47.3	0.39	15.4
	9	14.91	14.29	–0.62	95.84	0.78	5.4		
	10	19.18	18.69	–0.49	97.45	1.46	7.8	0.25	1.5
	11	39.86	37.70	–2.16	94.58	1.93	5.1		
	11	49.77	47.78	–1.99	96.00	2.18	4.6	1.62	3.8
Drinking water	11	0.50	1.06	0.56	212.00	0.19	18.1		
	11	0.69	0.65	–0.04	94.20	0.06	8.7	0.12	14.4
	12	1.99	3.05	1.06	153.27	0.39	12.8		
	11	2.97	3.01	0.04	101.35	0.22	7.2	0.33	10.8
	12	14.91	14.69	–0.22	98.52	0.62	4.2		
	12	19.18	20.05	0.87	104.54	0.88	4.4	0.46	2.7
	12	39.86	39.31	–0.55	98.62	1.67	4.3		
	12	49.77	48.93	–0.84	98.31	1.43	2.9	0.78	1.8
"Real" Wastewater	11	0.50	0.94	0.44	188.00	0.80	84.7		
	10	0.69	0.69	0.00	100.00	0.09	13.3	0.39	47.6
	10	1.99	3.00	1.01	150.75	0.38	12.7		
	10	2.97	3.01	0.04	101.35	0.20	6.6	0.23	7.8
	11	14.91	14.52	–0.39	97.38	0.66	4.6		
	11	19.18	19.26	0.08	100.42	0.77	4.0	0.77	4.6
	11	39.86	39.13	–0.73	98.17	1.78	4.6		
	11	49.77	49.17	–0.60	98.79	2.26	4.6	0.93	2.1

TABLE 6 Precision, Bias, and Matrix Recovery for Fluoride

Matrix	No. of Values	True Value	Mean Result	Bias Versus True Value	Recovery Versus True Value	Interlab Std Dev *S(t)*	Interlab %RSD	Single Operator Std Dev. *S(o)*	Analyst %RSD
Reagent water	10	0.50	0.51	0.01	102.00	11.00	11.4		
	10	0.71	0.73	0.02	102.82	7.90	8.1	0.02	2.9
	10	2.00	2.05	0.05	102.50	3.60	3.7		
	10	3.00	2.96	–0.04	98.67	4.40	4.6	0.09	3.4
	10	6.99	7.02	0.03	100.43	5.40	5.6		
	10	9.99	9.79	–0.20	98.00	4.60	4.8	0.13	1.6
	10	19.98	19.60	–0.38	98.10	3.80	3.9		
	10	24.99	24.51	–0.48	98.08	4.80	4.9	0.74	3.4
Substitute wastewater	10	0.50	0.50	0.00	100.00	0.09	18.0		
	10	0.71	0.71	0.00	100.00	0.09	12.0	0.01	2.3
	10	2.00	1.98	–0.02	99.00	0.12	6.0		
	10	3.00	2.94	–0.06	98.00	0.10	3.4	0.06	2.6
	10	6.99	6.92	–0.07	99.00	0.28	4.1		
	9	9.99	9.94	–0.05	99.50	0.46	4.7	0.28	3.3
	10	19.98	19.67	–0.31	98.45	0.94	4.8		
	10	24.99	24.78	–0.21	99.16	1.09	4.4	0.63	2.8
Drinking water	13	0.50	0.48	–0.02	96.00	0.06	12.9		
	13	0.71	0.68	–0.03	95.77	0.06	9.5	0.02	3.4
	13	2.00	1.96	–0.04	98.00	0.08	3.9		
	13	3.00	2.90	–0.10	96.67	0.10	3.4	0.08	3.5
	13	6.99	6.91	–0.08	98.86	0.25	3.6		
	13	9.99	9.91	–0.08	99.20	0.37	3.7	0.18	2.2
	13	19.98	19.94	–0.04	99.80	0.68	3.4		
	12	24.99	24.27	–0.72	97.12	1.63	6.7	1.30	5.9
"Real" Wastewater	11	0.50	0.47	–0.03	94.00	0.08	16.9		
	11	0.71	0.68	–0.03	95.77	0.08	11.7	0.04	7.6
	11	2.00	1.96	–0.04	98.00	0.12	6.3		
	11	3.00	2.93	–0.07	97.67	0.18	6.2	0.09	3.5
	11	6.99	6.85	–0.14	98.00	0.26	3.8		
	10	9.99	9.56	–0.43	95.70	0.73	7.7	0.44	5.3
	11	19.98	20.06	0.08	100.40	1.23	6.1		
	11	24.99	25.12	0.13	100.52	1.34	5.3	0.32	1.4

TABLE 7 Precision, Bias, and Matrix Recovery for o-Phosphate

Matrix	No. of Values	True Value	Mean Result	Bias Versus True Value	Recovery Versus True Value	Interlab Std Dev *S(t)*	Interlab %RSD	Single Operator Std Dev. *S(o)*	Analyst %RSD
Reagent water	10	0.50	0.41	–0.09	82.00	0.12	29.6		
	9	0.69	0.51	–0.18	73.91	0.13	26.6	0.03	7.2
	10	1.99	1.88	–0.11	94.47	0.16	8.3		
	10	2.98	2.76	–0.22	92.62	0.14	4.9	0.08	3.2
	10	14.86	14.93	0.07	100.47	0.64	4.3		
	9	19.80	19.76	–0.04	99.80	1.00	5.1	0.85	4.9
	10	39.60	39.79	0.19	100.48	1.38	3.5		
	10	49.51	50.10	0.59	101.19	1.76	3.5	0.72	1.6
Substitute wastewater	11	0.50	0.49	–0.01	98.00	0.15	30.0		
	10	0.69	0.59	–0.10	85.51	0.17	28.8	0.13	24.4
	11	1.99	1.92	–0.07	96.48	0.28	14.6		
	10	2.98	2.89	–0.09	96.98	0.22	7.6	0.18	7.5
	11	14.86	15.31	0.45	103.03	1.74	11.4		
	11	19.80	19.78	–0.02	99.90	1.16	5.9	0.84	4.8
	11	39.60	39.58	–0.02	99.95	2.72	6.9		
	11	49.51	49.19	–0.32	99.35	3.98	8.1	2.18	4.9
Drinking water	12	0.50	0.46	–0.04	92.00	0.14	30.0		
	13	0.69	0.55	–0.14	79.71	0.20	36.3	0.07	13.4
	13	1.99	1.89	–0.10	94.97	0.22	11.9		
	13	2.98	2.87	–0.11	96.31	0.24	8.5	0.07	2.8
	12	14.86	15.09	0.23	101.55	0.91	6.1		
	13	19.80	20.28	0.48	102.42	0.96	4.7	1.06	6.0
	13	39.60	40.37	0.77	101.94	2.15	5.3		
	13	49.51	50.75	1.24	102.50	3.14	6.2	1.03	2.3
"Real" Wastewater	11	0.50	0.43	–0.07	86.00	0.17	39.1		
	11	0.69	0.53	–0.16	76.81	0.24	46.5	0.12	25.8
	11	1.99	1.72	–0.27	86.43	0.27	15.8		
	11	2.98	2.52	–0.46	84.56	0.48	19.2	0.30	14.0
	11	14.86	14.93	0.07	100.47	0.91	6.1		
	11	19.80	19.90	0.10	100.51	1.35	6.8	0.91	5.2
	11	39.60	38.98	–0.62	98.43	1.45	3.7		
	10	49.51	48.26	–1.25	97.48	1.80	3.7	0.82	1.9

ANNEX

(Mandatory Information)

A1. Data

A1.1 All data presented in the following tables conform and exceed the requirements of Practice D 2777–98. Data from eleven reagent waters, eleven substitute wastewater, 15 drinking water, and thirteen wastewater sample matrices, were tested using a set of four Youden-Pair concentrations for seven analyte anions. All submitted individual data points are the average of duplicate samplings.

A1.2 Calibration Linearity

A1.2.1 All laboratories used a provided set of four certified, mixed anion calibration solutions in concentrations between 0.5 mg/L and 50 mg/L, formulated in random concentrations given in Table A1.1. They were prepared from certified, individual 1000 mg/L stock standards.[8] No dilution was necessary.

TABLE A1.1 Collaborative Calibration Standard, mg/L Concentrations

Analyte Anion	Standard 1	Standard 2	Standard 3	Standard 4
Chloride	50	25	0.5	10
Bromide	0.5	25	10	50
Nitrite	25	0.5	50	10
Sulfate	10	25	0.5	50
Nitrate	25	0.5	50	10
Fluoride	5	0.5	10	25
Phosphate	50	25	0.5	10

A1.2.2 A linear through zero regression was used to calculate the calibration curve. The range coefficient of determination (r^2) values obtained from the collaborative is shown in Table A1.2.

A1.3 Quality Control Solution Preparation

A1.3.1 The quality control solution (QCS) also was used as the calibration verification solution (CVS).

[8] Obtained from APG Inc., Belpre, OH.

TABLE A1.2 Expected Range of (r^2) Coefficient of Determination

Anion / r^2	Average, n=29	Lowest	Highest
Chloride	0.99987	0.99959	0.99997
Bromide	0.99953	0.99878	0.99996
Nitrite	0.99983	0.99961	0.99999
Sulfate	0.99976	0.99901	0.99999
Nitrate	0.99957	0.99840	0.99999
Fluoride	0.99972	0.99797	0.99999
Phosphate	0.99982	0.99942	0.99999

A1.3.2 The quality control solution (QCS) was manufactured and certified[8] as 100× concentrate, to replicate typical drinking water concentrations, and required 1:100 dilution with water before analysis. The QCS analyte concentrations, required control limits, and interlaboratory determined control limits based upon 82 analyses are given in Table A1.3.

A1.4 Youden Pair Spiking Solution Preparation

A1.4.1 Eight mixed anion, 100× concentrate, spiking solutions were prepared in accordance with the Reagents and Materials of the test method using anhydrous sodium salts. The mg/L concentrations of the eight standards followed the approved Youden Pair design: 0.5 and 0.7, 2 and 3, 15 and 20, 40 and 50 mg/L for all anions except fluoride, which is 0.5 and 0.7, 2 and 3, 7 and 10, 20 and 25 mg/L. The analyte true value concentrations were randomized among the eight spiking solutions as described in Table A1.4.

A1.4.2 A ninth solution containing approximately 10 mg/L of each analyte was used for method detection limit calculations.

A1.4.2.1 These solutions, kept at ambient temperature, were analyzed before and during the collaborative to monitor for accuracy and stability. The mg/L true value in was used to determine bias, matrix recovery, and the single operator and interlaboratory precision in the P and B tables in accordance with Practice D 2777.

A1.4.2.2 Solution 3 and 7 exhibited some conversion of nitrite to nitrate before analysis. This conversion is evident in the bias and % recovery for 0.5 mg/L and 2 mg/L nitrite and nitrate.

A1.5 Sample Matrix Preparation

A1.5.1 All participating laboratories provided and tested reagent water, substitute wastewater, naturally occurring drinking water, and naturally occurring wastewater. Before matrix spiking with the Youden Pair solutions, the sample matrix was evaluated, then appropriately diluted to give the highest anion concentration below 50 mg/L. The diluted sample matrix was used to dilute each Youden Pair spiking solution 1:100.

TABLE A1.3 Quality Control Acceptance Limits

Analyte Anion	True Value, mg/L	Certified Value, mg/L	Required 99 % Confidence Interval	Determined QCS Mean ± Std Dev, n = 82
Chloride	48.68	48.61 ± 0.12	43.99–52.96	47.64 ± 1.53
Bromide	0.00	0.00	0.00	0.00
Nitrite	2.87	2.90 ± 0.07	2.39–3.26	2.88 ± 0.19
Sulfate	35.69	35.63 ± 0.25	29.54–40.53	35.02 ± 1.21
Nitrate	15.76	15.78 ± 0.15	12.80–18.39	15.33 ± 4.35
Fluoride	1.69	1.68 ± 0.01	1.49–1.87	1.67 ± 0.09
Phosphate	5.47	5.55 ± 0.12	4.78–6.20	5.58 ± 0.28

TABLE A1.4 True Value Youden Pair Spiking mg/L Concentrations

Anion/TV	1	2	3	4	5	6	7	8	9
Chloride	0.71	2.00	2.98	14.92	39.81	19.91	49.76	0.50	10.20
Bromide	2.00	3.01	14.93	39.81	19.91	49.77	0.70	0.51	10.49
Nitrite	2.98	39.61	19.81	14.86	49.52	0.50	2.00	0.70	9.94
Sulfate	39.60	49.51	0.49	0.70	1.98	2.98	14.86	19.81	10.23
Nitrate	14.92	19.19	39.87	49.78	0.50	0.70	2.00	2.98	10.35
Fluoride	2.00	0.71	0.50	3.00	9.99	6.99	19.98	24.99	10.40
Phosphate	49.51	39.60	19.90	0.50	2.98	1.99	0.69	14.86	10.48

A1.5.2 Reagent water was used as-is. Substitute wastewater was diluted 1:20 with water. Naturally occurring drinking water was used as-is or diluted 1:5 with water. Naturally occurring wastewater was diluted between 1:3 and 1:20, except one which required a 1:1000 dilution due to high chloride.

A1.5.3 Due to the anion content of the naturally occurring drinking water and "real" wastewater matrices, some of the reported spike matrix results exceeded the scope of this test method. Linearity and matrix recovery data obtained from the collaborative indicated that these data are acceptable, and extended the useful range of this test method.

A1.5.4 Due to the anion content of the naturally occurring sample matrices given in Table A1.5, the low concentration bias and recovery may be misleading because of spiking a low anion concentration increment into a large naturally occurring concentration of the same anion.

A1.6 Test Method Detection Limits

A1.6.1 Spiking Solution No. 9, containing 10 mg/L of each analyte, was diluted 1:50 with water and was used for detection limit calculations. Seven replicate samplings were run, and the mean and standard deviation were calculated. The mean time corrected peak area response was given the true value of the solution No. 9, and from a simple proportion, the standard deviation was calculated as mg/L.

$$\text{Std Dev, mg/L} = \frac{(\text{True Value Conc Sol'n No. 9, mg/L})(\text{Response Std Dev})}{\text{Ave Response of Sol'n No. 9}} \quad \text{(A1.1)}$$

A1.6.2 Method detection limits were derived using EPA protocol and the student t-test at 6 df, as follows:

$$\text{The method detection limit (MDL)} = (3.14)(\text{Std Dev, mg/L}) \quad \text{(A1.2)}$$

A1.6.3 The upper and lower confidence limits were calculated as;

95 % Confidence Interval: LCL (Lower Confidence Limit) - 0.64 × MDL
UCL (Upper Confidence Limit) = 2.20 × MDL

A1.6.4 Method detection limits are given in Table A1.6.

TABLE A1.5 Blank Analyte Concentrations for Naturally Occurring Sample Matrices

Data in mg/L	Chloride	Sulfate	Nitrate
Drinking water	0.7 to 41.9	0.5 to 33.6	0.2 to 6.5
Substitute wastewater	20.5 to 25.5	3.2 to 4.0	Not Detected
"Real" wastewater	0.9 to 43.4	0.5 to 50.4	0.3 to 23.0

TABLE A1.6 Method Detection Limits

Anion	mg/L Solution Concentration	Method Detection MDL, mg/L	95 % Confidence Interval mg/L
Chloride	0.204	0.073	0.047 to 0.161
Bromide	0.210	0.132	0.084 to 0.290
Nitrite	0.199	0.102	0.065 to 0.223
Sulfate	0.205	0.066	0.042 to 0.145
Nitrate	0.207	0.082	0.052 to 0.180
Fluoride	0.208	0.032	0.020 to 0.070
Phosphate	0.210	0.102	0.065 to 0.224

APPENDIX

(Nonmandatory Information)

X1. SUGGESTED BACKGROUND REFERENCES

EPA Method 6500, "Dissolved Inorganic Anions in Aqueous Matrices by Capillary Ion Electrophoresis," *SW846*, Rev 0, January 1998.

Method 4140, "Inorganic Anions by Capillary Ion Electrophoresis," *Standard Methods for the Examination of Water and Wastewater*, 20th Edition, 1998, p. 4–12 to 4–20.

Krol, Benvenuti, and Romano, "Ion Analysis Methods for IC and CIA and Practical Aspects of Capillary Ion Analysis Theory," *Waters Corp., Lit Code WT-139*, 1998.

Jandik, P., Bonn, G., "Capillary Electrophoresis of Small Molecules and Ions," VCH Publishers, 1993.

Romano, J., Krol, J. "Capillary Ion Electrophoresis, an Environmental Method for the Determination of Anions in Water," *J. of Chromatography*, Vol 640, 1993, p. 403.

Romano, J., "Capillary Ion Analysis: A Method for Determining Ions in Water and Solid Waste Leachates," *Amer. Lab.*, May 1993, p. 48.

Jones, W., "Method Development Approaches for Ion Electrophoresis," *J. of Chromatography*, Vol 640, 1993, p. 387.

Jones, W., Jandik, P., "Various Approaches to Analysis of Difficult Sample Matrices for Anions Using Capillary Electrophoresis," *J. of Chromatography*, Vol 608, 1992, p. 385.

Bondoux, G., Jandik, P., Jones, W., "New Approaches to the Analysis of Low Level of Anions in Water," *J. of Chromatography*, Vol 602, 1992, p. 79.

Jandik, P., Jones, W., Weston, A., Brown, P., "Electrophoretic Capillary Ion Analysis: Origins, Principles, and Applications," LC·GC, Vol 9, Number 9, 1991, p. 634.

Romano, J., Jackson, P., "Optimization of Inorganic Capillary Electrophoresis for the Analysis of Anionic Solutes in Real Samples," *J. of Chromatography*, Vol 546, 1991, p. 411.

Jandik, P., Jones, W., "Optimization of Detection Sensitivity in the Capillary Electrophoresis of Inorganic Anions," *J. of Chromatography*, Vol 546, 1991, p. 431.

Jandik, P., Jones, W., "Controlled Changes of Selectivity in the Separation of Ions by Capillary Electrophoresis," *J. of Chromatography*, Vol 546, 1991, p. 445.

Foret, R., et.al., "Indirect Photometric Detection in Capillary Zone Electrophoresis," *J. of Chromatography*, Vol 470, 1989, p. 299.

Hjerte'n, S. et. al., "Carrier-Free Zone Electrophoresis, Displacement Electrophoresis and Isoelectric Focusing in an Electrophoresis Apparatus," *J. of Chromatography*, Vol 403, 1987, p. 47.

Serwe, M., "New ASTM Standard: Recommended Operating Conditions for the Agilent CE," Agilent Technologies Application Brief, Publication # 5968–8660E.

Method for the Determination of Radium-228 and Radium-226 in Drinking Water by Gamma-ray Spectrometry Using HPGE or Ge(Li) Detectors

December, 2004

Environmental Resource Center
Georgia Institute for Technology
Atlanta, GA

Revision 1.2

Acknowledgements

The Environmental Resources Center (ERC) would like to recognize the work contributed by the following individuals in the development, preparation and validation of this method. At ERC, James Gary for sample preparation, Dave Crowe for sample counting, Cliff Blackman for software assistance and Brad Addison at State of Georgia Department of Natural Resources, Drinking Water Program for contract support. Finally, at New Jersey Department of Health and Senior Services Laboratory, Bahman Parsa, Gail Suozzo, Reynaldo Obed and William Nemeth for their assistance by acting as a second laboratory to validate this method.

Table of Contents

I-1. Introduction

To lower the cancer risks of the consumers of drinking water provided by Public Water Supplies (PWSs), the Safe Drinking Water Act (SDWA) requires PWSs to measure, at a minimum, the gross alpha particle activity of their finished water at specific intervals appropriate to the specific local conditions of each water supply. Additionally, concern related to the radium-228 (Ra-228) content of drinking waters has resulted in the requirement finished waters intended for public consumption from PWSs be analyzed for this carcinogen, in addition to the gross alpha particle activity, beginning with the compliance monitoring period starting on December 8, 2003. If the gross alpha radioactivity measured for a PWS is above 5 pCi/L, then the measurement of the regulated contaminant, radium-226 (Ra-226) is also required. These requirements will have the consequence of a tremendous increase of the number Ra-228 measurements that must be made, as well as the likelihood both Ra-226 and Ra-228 must be measured in the same sample, increasing the number of measurements required.

While other EPA-approved radium methods can provide sufficient accuracy and precision for the purposes of the SDWA monitoring program, they all share the general assessment by radiochemists after using them that they are labor intensive and time consuming. They all require several isolation and purification steps involving sequential precipitations from analytically large volumes, then possibly liquid-liquid extractions (depending on the particular method). They all end with a final preparation step for measurement either by gas proportional counting (EPA 903.0, EPA 904.0, etc), or by evolving a gaseous daughter product from the radionuclide of interest from the sample, then measuring it with an alpha scintillation detection system (EPA 903.1, etc). Additionally, training periods for technicians performing these methods are long because of the numerous steps and the time involved in performing these analyses, increasing their overall cost.

This draft method has been developed in an effort to provide a more cost-effective alternative that reduces the labor and time required for processing samples for these analyses. It utilizes the initial precipitation steps found in the approved methods, but utilizes gamma-ray spectrometry techniques for detection and quantitation using High Purity Germanium (HpGe) detectors. Lithium-drifted Germanium (Ge(Li)) detectors may also be used, but will require larger volumes of sample since they have lower detection efficiencies than the HpGe detectors. Unlike sodium iodide gamma-ray detectors, these solid state detectors have sufficient spectral resolution so that peaks unique to the daughter progeny of Ra-226 and Ra-228 can be quantitatively measured in shorter count times typically used for gas proportional measurements of these regulated contaminants.

1.0 Scope and Application

1.1 This method describes the measurement of Radium-226 (Ra-226, CAS Registry No.13982-63-3) and Radium-228 (Ra-228, CAS Registry No. 15262-20-1) in finished drinking water matrices in the same compliance monitoring sample. This method can also be used to measure them separately if only one of these analyses is required. These data may be used in the Environmental Protection Agency's (EPA's) data gathering and monitoring programs under the Safe Drinking Water Act. It utilizes the initial precipitation steps for these analytes found in methods 903.0, 904.0, Ra-05, and other similar methods, but uses gamma-ray spectrometry techniques for detection and quantitation instead of gas proportional counting. Analytical test conditions are selected to ensure the required detection limit of 1 pCi/L can be achieved routinely according to the capabilities of each laboratory that chooses to utilize this method. Since the method of detection's calibration efficiency is linear with respect to intensity, it has a quantitative analytical range of several orders of magnitude.

1.2 Each laboratory that uses this method must demonstrate the ability to generate acceptable results using the procedure in Section 9.2.

2.0 Summary of Method

2.1 An aliquant from a sample (whose volume is appropriate for the efficiency of the detector and projected count time so that a detection limit of 1 pCi/L can be achieved) is poured into a borosilicate beaker sufficiently large to hold the entire sample. A solution of barium chloride is added to the aliquant of sample to serve as carrier. The sample is then stirred and heated to boiling. Concentrated sulfuric acid is added to the heated sample and radium is collected by coprecipitating it as a sulfate.

2.2 The precipitate is collected on preweighed filter paper, then dried and reweighed to obtain a net weight of precipitate to assess the chemical efficiency of the coprecipitation. The filter paper holding the precipitate is placed into containers whose geometry is appropriate for the type of gamma-ray detector being used.

2.3 The prepared samples can either be directly measured for their Ra-228 content, or set aside for a minimum ingrowth period appropriate for each measurement (from 5 days to 2 weeks for Ra-226, or both measurements). After the necessary ingrowth period, the sample is counted with a gamma-ray spectrometry system to determine the content of the regulated contaminants for a count time previously determined to achieve the required detection limit.

2.4 Quality is assured by repeated testing of the precipitation, counting, and gravimetric systems.

3.0 Definitions

3.1 Definitions for terms used in this method are given in section 18, Glossary of Definitions and Purposes.

4.0 Interferences

4.1 Reagents, glassware, and other sample-processing hardware may yield artifacts that affect results. Specific selection of reagents is required to ensure no traces of the analytes are present. The glassware and sample processing hardware is cleaned by washing in hot water and a detergent designed to remove radioactive compounds, then rinsing them in tap water, and a final rinse in deionized water. All glassware must also receive an acid rinse to ensure contaminant removal and to hydrate the outer layers of silica, making them more resistant to contamination. This is followed by a final rinse in deionized water.

4.2 All materials used in the analysis shall be demonstrated to be free from interferences under the conditions of analysis by running laboratory blanks as described in Section 9.4.

4.3 Excess barium and strontium in the drinking water sample can result in high chemical yields, sometimes exceeding 100 percent recovery. Since their concentrations are restricted in finished drinking water to low

levels, the related bias would only be a concern if this method is used to measure source or waste waters.

4.4 Interferences separated from samples will vary considerably from source to source, depending upon the diversity of the site being sampled.

5.0 Safety

5.1 The toxicity or carcinogenicity of each reagent and radioactive standards used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals and radioactive standards should be reduced to the lowest possible level. It is suggested that the laboratory perform personal hygiene monitoring of each analyst using this method, and all analysts should wear radiation dosimetry badges while performing this method to monitor their exposure to ionizing radiation. The results of this monitoring must be made available to the analyst.

5.2 Sample containers should be opened in a restricted area with caution and handled with gloves to prevent exposure.

5.3 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. Additional information on laboratory safety can be found in References 16.4–16.6.

5.4 Diethyl ether (also referred to as "ethyl ether") is an extremely flammable solvent, and may form explosive peroxides during storage. Diethyl ether also is considered a skin, eye, and respiratory irritant. This reagent should be used in a well ventilated area (e.g., a fume hood), kept away from ignition sources, and handled by analysts wearing appropriate protective-wear (e.g., safety glasses or goggles). For additional information on this substance please consult the Material Safety Data Sheet (MSDS) for diethyl ether.

6.0 Equipment and Supplies

Note: Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.

6.1 Sampling equipment.

6.1.1 Sample collection bottles—Plastic, with screw cap. Sample collection bottles should be of an appropriate volume to minimize the number of containers required per sample. Each sample must have a minimum of 4 aliquants of volume available so they may be available to be used as a batch QC sample and have at least one aliquant available in the event retesting becomes necessary.

6.1.2 Bottles and lids must be lot-certified to be free of artifacts by running laboratory blanks according to this method (per Section 9.4).

6.2 Equipment for glassware cleaning.

6.2.1 Laboratory dishwasher. If one is not available, then the laboratory must have a dishwashing station set up consisting of the minimum of a sink for washing and rinsing glassware, and a drying rack.

6.2.2 A nonmetallic tub or vat with a minimum volume of 30 L to hold the acidic solutions used for acid rinsing. It must also have a cover that can be placed over it when it is not in use.

6.2.3 A source of ASTM Type 2 reagent water to use for a final rinse for glassware.

6.3 Equipment for calibration.

6.3.1 Analytical balance—a readability of 0.01 mg is required.

6.3.2 Volumetric flasks—Glass, 100 mL, 500 mL, 1000 mL and 2000 mL

6.3.3 Bottles—Assorted sizes, with PTFE-lined screw caps reagent storage

6.3.4 Volumetric pipettes—Glass, 1 mL, 5 mL

6.3.5 Gamma-ray spectrometry system utilizing either High Purity Germanium (HPGe) or lithium drifted germanium (Ge (Li))detectors.

6.4 Equipment for sample precipitation.

6.4.1 Beaker—must be made of a heat resistant borosilicate glass and capable of holding the volume of sample necessary to reach the required detection limit.

6.4.2 Heated magnetic stirrer

6.4.3 PTFE-coated magnetic stirring bars

6.4.4 Volumetric flasks 2000 mL

6.5 Equipment for collecting precipitate.

6.5.1 Filtering apparatus— 25 mm or 47 mm diameter filter funnel that is mounted on either a manifold connected to a vacuum source or to a vacuum flask that is connected to a vacuum source.

6.5.2 Filter paper— Membrane, 0.45 μm porosity, 25 mm or 47 mm diameter, whichever is appropriate for the filter funnel.

6.5.3 Sample containers for the selected geometry, such as stainless steel planchets, plastic Petri dishes or vials of the appropriate size to fit into the well of a deep well gamma-ray detector

6.5.4 Drying lamp

6.6 Equipment for yield determination.

6.6.1 Analytical Balance— a readability of 0.01 mg is required.

6.7 Equipment for counting gamma rays from analytes.

6.7.1 Gamma-ray spectrometry system utilizing either High Purity Germanium (HPGe) or lithium-drifted germanium (Ge(Li))detectors.

7.0 Reagents and Standards

7.1 Reagent water—Standard Methods (see reference 16.2) requires reagent water for radiochemistry methods meet the requirement specified as ASTM Type 2 reagent water. Distilled water, deionized water or water prepared by passage of tap water through activated carbon have been shown to be acceptable sources of reagent water. The reagent water's resistivity must be checked prior to its use to prepare samples or standards to ensure it is of adequate quality for use with this method.

7.2 Hydrochloric acid, HCl (12 N)

7.3 Sulfuric acid, H_2SO_4 (18 N) : cautiously add, with stirring, 500 mL 36 N H_2SO_4 to 400 mL water and dilute to 1 L.

7.4 Ethanol—ACS, residue less than 1 mg/L.

7.5 Diethyl ether.

7.6 Nitric Acid, HNO_3 (16 N)

7.7 Barium carrier Ba^{++} - 9 mg/mL. Dissolve 16.01 grams of Ba $Cl_2 - 2\ H_2O$ in water, add 5 mL 16 N HNO_3, and dilute to 1 L with reagent water.

7.8 Ra-226 spiking standard solution; for matrix spikes and matrix spike duplicates.

7.8.1 Use a NIST traceable Ra-226 standard when available that is from a different source than the one used to prepare the efficiency calibration standard

7.8.2 The calibration certificates for these standardized solutions most often report their concentrations as an activity per volume weight. When extracting the standard solution from the container it arrives in, the total net weight of solution should be measured to ensure the reported total activity is accurate.

7.8.3 Before diluting it, calculate a final dilution volume that will provide an activity between 5 and 10 pCi/mL.

7.8.4 Use a Class a volumetric flask that will contain all the calculated final volume.

7.8.5 Use a diluent that has the same molar concentration and is of the same type of acid used to produce the original standardized solution.

7.8.6 Pour approximately 75 percent of the diluent into the volumetric flask.

7.8.7 Weigh the standard in its original container.

7.8.8 Remove the standardized solution from the balance and pour its contents into the volumetric flask. Wash the original container three times with some of the remaining diluent, and pour these washings into the volumetric flask.

7.8.9 Wash the original container with ethanol to remove any remaining rinse solution and discard it since it should not have any activity. Set aside to dry. Once dry, record its weight.

7.8.10 Slowly bring the volume of diluted solution in the volumetric flask up to the white line that represents its calibrated volume. Ensure the final volume is not above this line.

7.8.11 Subtract the weight of the empty original container from the weight of the container and original solution. Compare this to the weight reported on the calibration certificate.

7.8.12 If different, use the determined net total weight of the standardized solution and multiply it by the activity per gram reported on the calibration certificate, then divide it by the volume of diluent in the final working solution. Use this result when using a final activity per mL for the standard.

7.9 Ra-228 Standard spiking solution. Use the same steps as in section 7.8 used to prepare the Ra-226 standard spiking solution.

7.10 Alternate Carrier: Pb^{2+} Carrier – 20 mg/mL. Dissolve 32 g of $Pb(NO_3)_2$ in water. Add 5 mL 16N HNO_3 and dilute to 1 L with reagent water.

8.0 Sample Collection, Preservation, and Storage

8.1 Collect a sufficient volume of sample so that a minimum of 4 aliquants of sample can be prepared from it. This provides sufficient volume that a sample, a Matrix Spike (MS) and Matrix Spike Duplicate (MSD) pair may be prepared from each collected sample, with one aliquant volume left for reserve in case the sample must be remeasured. Plastic bottles or cubitainers may be used to collect the sample following conventional sampling procedures.

8.2 Once collected, samples for these analyses must be preserved within 5 days of collection by adding sufficient concentrated nitric acid so that the collected sample has a pH of less than 2 as specified in Table 17.2.

8.3 All samples must be analyzed within prescribed maximum holding time after collection in Table 17.2.

9.0 Quality Control

9.1 Each laboratory that uses this method is required to operate a formal quality assurance program (Reference 16.8). For each method the laboratory uses to report compliance monitoring results, the minimum requirements of this program consist of an initial demonstration of analyst capability, ongoing analyses of

standards and reagent blanks as a test of continued accuracy and freedom from interferences, and analyses of matrix spike (MS) and matrix spike duplicate (MSD) samples to assess precision and provide an additional metric of accuracy. Laboratory analyst performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1.1 The analyst shall make an initial demonstration of ability to generate acceptable accuracy and precision with this method. This ability is established as described below.

9.1.2 Each sample analytical batch must include Quality Control (QC) samples to demonstrate the overall accuracy, precision and freedom from interferences for the analyses. Analysis of a Matrix Spike (MS) is done to demonstrate accuracy. Precision can be demonstrated by using a second aliquant of the sample selected to produce the MS to produce a Matrix Spike Duplicate (MSD). The criteria for spiking samples are described in Section 9.3.

9.1.3 Alternatively, the MSD may be replaced by using a second aliquant of a sample to duplicate the measurement (DUP), then comparing their results to assess precision. The criteria for duplicating samples are described in Section 9.4.

9.1.4 An analysis of a Reagent Blank (RB) is required to demonstrate the reagents, sample processing glassware, and workspace are free from contamination that will interfere with the measurements of the samples in each analytical batch. The results of RBs shall be recorded and monitored to ensure interferences in the analysis system remain in control. The criteria for RBs are described in Section 9.5.

9.1.5 The laboratory shall demonstrate calibration verification for each analytical batch of samples by measuring a Laboratory Fortified Blank (LFB). The results of the LFBs shall be recorded and monitored to ensure the analysis system remains in control. These procedures are described in Section 9.6.

9.1.6 The laboratory must maintain records to define the quality of data that is generated. Development of accuracy statements should be completed as described in Sections 9.3.7 and 9.6.3.

9.1.7 For this procedure, a sample preparation batch is a set of samples precipitated at the same time, and must not exceed 20 samples. Each sample preparation batch must also include the four Quality Control samples described in sections 9.1.2. though 9.2.5 for a maximum number of samples in each sample preparation batch of 24. If greater than 20 samples are to be precipitated at one time, the samples must be separated into two sample preparation batches of 20 or fewer samples.

9.2 Initial Demonstration of Laboratory Capability

9.2.1 Initial precision and recovery (IPR)—To establish the ability to generate acceptable precision and accuracy, the analyst shall perform the following operations:

9.2.1.1 Prepare four samples by using 4 to 8 L of ASTM type I or II deionized water and add a sufficient volume of Ra-226 and Ra-228 standard spiking solutions so that both radioanalyte concentrations are between 5 and 10 times their required detection limits. Divide the volumes equally into four aliquants.

9.2.1.2 Using the results of the set of four analyses, compute the average percent recovery (P_{av}) and the standard deviation of the percent recovery (s) for Ra-226 and for Ra-228 (if determined). Use the following equation for calculation of the standard deviation of the percent recovery:

$$P_{av} = \frac{1}{n}\sum_{i=1}^{n} P_i \quad \text{and} \quad s = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(P_i - P_{av})^2} \qquad (1)$$

where:

n = number of samples
P_i = percent recovery for each sample
P_{av}= average percent recovery for all samples
s = standard deviation of the percent recovery

9.2.1.3 Compare s and P_{av} with the corresponding limits for initial precision and recovery in Table 17.1. If s and P_{av} meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the precision limit or P_{av} falls outside the range for recovery, system performance is unacceptable. In this event, correct the problem and repeat the test.

9.3 Matrix Spikes

9.3.1 The laboratory must spike, in duplicate, a minimum of 5 percent of all samples (one sample in each batch of twenty samples. The two sample aliquants shall be spiked with the Ra-226 and Ra-228 spiking solutions.

9.3.1.1 Prepare a spiking solution that will produce an activity concentration between 3 and 5 pCi/L (between 3 times the required detection limit and the combined MCL for these radioanalytes) when added to each aliquant selected for spiking.

9.3.1.2 Analyze the first sample aliquant according to the procedure beginning in Section 11 to determine the background concentration of Ra-226 and Ra-228.

9.3.1.3 Spike the two aliquants selected for spiking, then also measure them according to the procedure beginning in Section 11.

9.3.1.4 Calculate the percent recovery (P) of Ra-226 and Ra-228 in each aliquant using the following equation:

$$P = \frac{(A - B) \times 100\,\%}{T} \qquad (2)$$

where:

A is the total activity concentration of the analyte of interest
B is the background concentration of the analyte of interest
T is the activity concentration of the analyte added to the sample

9.3.1.5 Compare the percent recovery of the Ra-226 and Ra-228 with the corresponding QC acceptance criteria in Table 17.1.

9.3.1.6 If the results of the spike fail the acceptance criteria, and the recovery of the QC standard in the ongoing precision and recovery test (Section 9.6) for the analytical batch is within the acceptance criteria in Table 17.1, an interference is present. In this case, the result may not be reported for regulatory compliance purposes and the analyst must assess the potential cause for the interference. If the interference is attributable to sampling, the site or discharge should be resampled. If the interference is attributable to a method deficiency, the analyst must modify the method, repeat the tests required in Section 9.1.2, and repeat the analysis of the sample and the MS/MSD.

9.3.1.7 If the results of both the spike and the ongoing precision and recovery test fail the acceptance criteria, the analytical system is judged to be out of control, the problem shall be identified and corrected, and the sample shall be reanalyzed.

9.4 Precision Assessments

Compute the relative percent difference (RPD) between the two results of either the sample and its duplicate measurement or between the Matrix Spike and the Matrix Spike Duplicate (not between the two recoveries) using the following equation:

$$RPD = \frac{|A_1 - A_2|}{(A_1 + A_2)/2} \times 100\,\% \qquad (3)$$

where:

A_1 is the concentration of Ra-226 or Ra-228 in the sample

A_2 is the concentration of Ra-226 or Ra-228 in the second (duplicate) sample

9.4.2 The relative percent difference for the duplicate measurements shall meet the acceptance criteria in Table 17.1. If the criteria are not met, the analytical system is judged to be out of control, and the problem must be immediately identified and corrected, and the analytical batch reanalyzed.

9.4.3 As part of the QC program for the laboratory, method precision and accuracy for samples should be assessed and records should be maintained. After the analysis of five spiked samples in which the recovery passes the test in Section 9.3.4, compute the average percent recovery (P_a) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $P_a - 2s_p$ to $P_a + 2s_p$. For example, if $P_a = 90$ % and $s_p = 10$ % for five analyses of Ra-226 and for Ra-228, the accuracy interval is expressed as 70 %–110 %. Update the accuracy assessment on a regular basis (e.g., after each five to ten new accuracy measurements).

9.5 Reagent Blanks for Contamination Checks

9.5.1 Reagent water blanks are analyzed to demonstrate freedom from contamination.

9.5.2 Precipitate a sample prepared with laboratory reagent water using the same volume as samples with each analytical batch. The blank must be subjected to the same procedural steps as a sample.

9.5.3 If material is detected in the blank at a concentration greater than the Minimum Level required by EPA of 1 pCi/L, analysis of samples is halted until the source of contamination is eliminated and a blank shows no evidence of contamination. All samples must be associated with an uncontaminated method blank before the results may be reported for regulatory compliance purposes.

9.6 Laboratory Fortified Blanks for Ongoing Precision and Recovery Assessments

9.6.1 One sample shall be prepared with reagent water that is spiked with a known amount of analyte to assess the Ongoing Precision and Recovery method performance that is independent of matrix effects.

9.6.1.1 Precipitate a spiked aliquant of laboratory reagent water at the same volume as samples with each analytical batch. This Laboratory Fortified Blank (LFB) must be subjected to the same procedural steps as the samples.

9.6.1.2 Spike the LFB with enough Ra-226 and Ra-228 so the activity concentration is approximately 5 pCi/L .

9.6.1.3 Evaluate using Equation 2 where $B = 0$.

9.6.2 Compare the concentration with the limits for ongoing precision and recovery in Table 17.1. If the concentration is in the range specified, the analytical processes are in control and the analysis of

samples are acceptable. If, however, the concentration is not in the specified range, the analytical process is not in control. In this event, correct the problem, re-extract the analytical batch, and reevaluate the ongoing precision and recovery sample for acceptability.

9.6.3 The laboratory should add results that pass the specification in Section 9.6.2 to IPR and previous OPR data and update QC charts to form a graphic representation of continued laboratory performance. The laboratory should also develop a statement of laboratory data quality for each analyte by calculating the average percent recovery (R) and the standard deviation of the percent recovery (s_r). Express the accuracy as a recovery interval from $R - 2s_r$ to $R + 2s_r$. For example, if $R = 95$ % and $s_r = 5$ %, the accuracy is 85 % to 105 %.

9.7 The specifications contained in this method can be met if the apparatus used is scrupulously cleaned and dedicated for the determination of Ra-226 and Ra-228. The standards used for initial precision and recovery (IPR, Section 9.2.2), matrix spikes (MS/MSD, Section 9.3), and ongoing precision and recovery (OPR, Section 9.6) should be identical, so that the most precise results will be obtained. However, they musty not be from the same source used for calibration standards.

9.8 Depending upon specific program requirements, field replicates and field spikes of the analytes of interest into samples may be required to assess the precision and accuracy of the sampling and sample transporting techniques.

10.0 Calibration and Standardization

10.1 Analytical balance calibration

10.1.1 The analytical balance must be calibrated annually using NIST –traceable weights.

10.1.2 Prior to use for this method the calibration for the balance must be checked with 1mg and 1000 mg weights from a Class S set.

10.1.3 Calibration shall be within ± 10 % (i.e. ±0.1 mg) at 1 mg and ± 0.5 % (i.e. ±5 mg) at 1000 mg. If values are not within these limits, recalibrate the balance.

10.2 Carrier standardization

10.2.1 In triplicate in a 100 mL beaker to 20 mL DI H_2O pipet 5 mL of barium carrier. Add 5 drops of concentrated HCl. If the laboratory prefers to use a lead carrier, substitute 10 mL of lead carrier in place of the barium carrier.

10.2.2 Heat to boiling and add 20 mL 18 N H_2SO_4 with stirring.

10.2.3 Digest 5–10 minutes and then let solution cool.

10.2.4 Slurry precipitate and transfer to a 100 mL centrifuge tube using 0.1 N H_2SO_4 as a wash.

10.2.5 Wash precipitate twice with 10 mL 0.1 N H_2SO_4 and discard washes.

10.2.6 Transfer precipitate to a preweighed sintered glass crucible and dry at 110°C for two hours.

10.2.7 Place in desiccator to cool.

10.2.8 Weigh, Record gross and net weight for use in calculating barium (or lead) weight per mL.

10.3 Gamma-ray Detector Calibration

10.3.1 Laboratories may choose to follow the energy and efficiency calibration procedures for gamma-ray detectors as described in EPA method 901.1. Provisions must be made to ensure calculations in data reduction spreadsheets and software are able to adjust sample measurements for systematic interferences to gamma-ray measurements. Specifically software must correct for the summation effect observed for the 609 keV photopeak from Bi-214. If not, then the following steps must be followed to calibrate the gamma-ray detector for energy and efficiency.

10.3.2 Energy Calibration

10.3.2.1 Follow the instrument manufacturer's instructions for powering up and adjusting the electronics of the gamma-ray detector system. A gamma-ray spectral window extending to a minimum of 2000 keV is required for this method.

10.3.2.2 Obtain and measure a NIST-traceable source that contains a minimum of 6 photopeaks that extend throughout the spectral range selected for use by the laboratory. Since the energy response for gamma-ray detectors is not affected by geometry, this energy calibration source need not be in the same geometry used for sample measurements. Count time used for energy calibrations only need to be long enough so the lowest activity peaks used for calibration are distinct and well defined from the Compton background.

10.3.2.3 From the acquired spectra, determine the channel number where the maximum (i.e. the peak centroid) for each peak occurs either by manual inspection and calculation, or manufacturer supplied data reduction software. Record each peak centroid and channel number pair.

10.3.2.4 Using a calculation spreadsheet or manufacturer supplied software, determine the relationship for the peak energy/centroid pairs by plotting them or fitting a mathematical formula to them.

10.3.3 Efficiency Calibration with a prepared efficiency source. Measuring a source prepared in the same way as the samples and measured in the same geometrical orientation distance from the detector as the samples produce the most accurate measurement of the efficiency for the peaks originating from the Ra-226 and Ra-228 progeny.

10.3.4 Efficiency calibration source preparation.

10.3.4.1 Obtain NIST traceable solutions of Ra-226 and Ra-228.

10.3.4.2 Pipet 5 mL of barium carrier into a small beaker, then add 5 drops of concentrated HCl and 20 mL of deionized water.

10.3.4.3 Add appropriate amounts of NIST traceable solutions of Ra-226 and Ra-228 with a calibrated autopipette or glassware so that source count times will be no longer than the count times for samples, but not so high that instrument dead time will exceed 5 percent. Calculate the decays per minute for each radioanalyte.

10.3.4.4 Heat the contents of the beaker to boiling, then add 20 mL 18 N H_2SO_4 while stirring the contents of the beaker.

10.3.4.5 Digest 5- 10 minutes and then let solution cool.

10.3.4.6 Slurry precipitate and transfer to a centrifuge tube using 0.1 N H_2SO_4 as a wash.

10.3.4.7 Wash precipitate twice with 10 mL 0.1 N H_2SO_4. Centrifuge between washes and discard the washes.

10.3.4.8 Obtain a filter of the same type and size to fit inside the sample containers selected for use to make sample measurements. Tare the filter by weighing it to an accuracy of 0.01 mg.

10.3.4.9 Place the filter in an appropriate sized filtering funnel mounted on a vacuum manifold.

10.3.4.10 Filter with suction through the tared filter. Quantitatively transfer precipitate to the filter by rinsing the remaining particles from the beaker with a jet of reagent water.

10.3.4.11 Dry the precipitate on the filter with 10 mL ethanol, followed by 10 mL

diethyl ether.

10.3.4.12 Weigh filter and precipitate to determine yield.

10.3.4.13 Place filter in the same type of sample container that will be used for samples.

10.3.4.14 Hold for a minimum of 4 weeks so the radium progeny can approach full ingrowth prior to gamma-ray spectral analysis with a germanium detector.

10.3.5 Efficiency Source Measurement

10.3.5.1 This calibration is performed with the same counting geometry as the samples. After ingrowth, place the prepared efficiency source into the sample cave in the same orientation and distance from the germanium detector as will be used for sample measurement.

10.3.5.2 Count the efficiency source for a long enough count time so that the peaks selected to use for sample measurements (the 338, 352, 609 and 911 keV photopeaks) will have accumulated at least 10,000 net counts above the Compton background.

10.3.5.3 After the measurement count time is complete, obtain the net counts for the peaks referenced in the previous step using commercially available gamma-ray data analysis software or a calculation spreadsheet.

10.3.5.4 Calculate the efficiency (ε) individually for each photopeak using the following calculation;

$$\varepsilon = \frac{C}{D \times T \times R \times F}$$

where:

C = Net counts

D = Calibrated decays per minute (DPM) for the photopeak from step 10.3.3.1.3.

R = Fractional chemical yield of barium carrier from step 10.3.1.12.

T = Count time (in minutes)

F = Fractional intensity of the photopeak

10.4 Detector Background Characterization. The laboratory must determine the background activity that occurs in the regions of interest for each photopeak used to measure the radium isotopes in each gamma-ray detector used to make measurements for the method before it can be implemented on a routine basis.

10.4.1 Place a sample container containing a clean filter of the same type and size that will be used for sample measurements into the gamma-ray detector cave. Ensure it is in the same orientation and distance from the detector as will be used for sample measurements.

10.4.2 Measure the sample container and filter for a sufficiently long count time to determine if there is any activity in the regions of interest for the photopeaks used to measure the radium isotopes. A minimum count time of 36000 seconds is recommended.

10.4.3 Examine the regions of interest used for the radium measurements to see if there is a net activity noted in them. If net activities are noted, use them in Step 11.2 in the next section to determine if they are sufficiently low so that reasonable count times and sample volumes can be used to reach the required sensitivities for each radium isotope measured with this method.

10.4.4 If the background is determined to be excessive, see if this background can be reduced by cleaning the interior of the gamma-ray detector cave, removing samples from the count room, venting the liquid nitrogen exhaust into the sample cave to displace any radon present, or adding additional shielding to the gamma-ray detector cave, then repeat steps 10.4.1 though 10.4.3

10.4.5 If the background is determined not to be excessive, store the background measurement

electronically for later use in data reduction.

10.4.6 At least monthly, repeat steps 10.4.1 through 10.4.5 and record the activities for each region of interest used to measure the radium isotopes. The laboratory should then control chart the results and set control limits for the backgrounds in each region of interest to ensure their background activities remain in control for sample measurements.

11.0 Procedure

This method is entirely empirical. Precise and accurate results can be obtained only by strict adherence to all details.

Note: *The procedure below is based on the preparation, precipitation, and analysis of a 2 L sample volume and a nominal 40 % efficiency high purity germanium detector. If a different detector is used for analysis, the laboratory may need to adjust the volume of sample and counting time required to reach the desired detection limit.*

11.1 Determine the sample volume, ingrowth period and count time required to meet the required detection limits.

11.1.1 The sensitivity of these measurements must comply with the required detection limits for these radioanalytes specified at 40 CFR part 141.25(c), Table 1 as 1 pCi/L for both radium isotopes.

11.1.2 A minimum ingrowth period of 14 days is recommended for Ra-226 measurements.

11.2 Radium purification.

11.2.1 Measure the volume of preserved drinking water sample (Note 1), determined in step 11.1 in a volumetric flask or graduated cylinder, then pour the measured volume into a borosilicate beaker large enough to contain it.

11.2.2 Add 10 mL of 12 N hydrochloric acid for every liter of sample used and stir.

11.2.3 Using a volumetric pipet add 5.0 mL barium carrier (9 mg/mL). If the lead carrier is being used instead, add 10.0 mL lead carrier (20 mg/mL) in place of the barium carrier.

11.2.4 Stir and heat to boiling.

11.2.5 Precipitate barium sulfate by adding 10 mL of 18 N H_2SO_4 for every liter of sample used, stirring frequently. Boil for 30 min.

11.2.6 Store overnight to let the precipitate settle, or for fast settling cool 30 min in an ice bath.

11.2.7 Obtain a filter of the size appropriate for the filtering funnel (Note 2) used at the laboratory. Tare the filter by weighing it to the nearest 0.01 mg.

11.2.8 Place the tared filter into a filter funnel that is attached to a vacuum manifold or to a vacuum flask that is connected to a vacuum source.

11.2.9 Filter with suction through the tared filter. Quantitatively transfer precipitate to the filter by rinsing the remaining particles from the beaker with a jet of water.

11.2.10 Dry the precipitate on the filter with 10 mL ethanol, followed by 10 mL diethyl ether.

11.2.11 Weigh filter and precipitate. Record the weight.

11.2.12 Subtract the tared filter weight from the combined weight of the filter and precipitate to determine the net weight of the precipitate. Divide this net weight of the precipitate by the maximum theoretical weight of the precipitate based on the amount of barium carrier that is used for the precipitation. The ratio is the Fractional Chemical Yield (Y) for the sample precipitation.

11.2.13 Place the filter in the same type of sample container as the efficiency calibration standard.

11.2.14 Repeat steps 11.2.1 for each sample in the preparation batch.

11.2.15 Hold the prepared samples for Ra-226 progeny ingrowth before proceeding to the next step. If only Ra-228 measurements are to be made for the prepared samples, then proceed directly to the next step. Calculate the ingrowth by the following equation:

Ra-226 progeny ingrowth = $1 - e^{-\lambda t}$

Where;

t is time in days and λ is ln(2) divided by the half-life in days of 3.825 = 0.18112 d^{-1} (or one can interpolate from Table 17.3)

Note 1: At the time of sample collection, add 4 mL 16 N HNO_3 for each gallon (3.7 L) of water.

Note 2: A 47 mm filter is used with a steel planchet or plastic Petri dish (step 11.1.8) but other filters can be substituted, subject to step 11.2.1, such as a 25 mm filter for placement in ring and disk or filters of various sizes for placement in vial to be counted in well type detector.

11.3 Sample Measurement

11.3.1 Place the sample container and filter assembly in the same geometry as was used for measuring the efficiency source in step 10.3.5. Collect the gamma-ray spectra for the count time determined in step 11.1.

11.3.2 Use either manufacturer supplied software or a calculation spreadsheet to determine the net activity in the regions of interest for each photopeak used to measure the radium isotopes. Ensure it will:

11.3.2.1 Subtract the Compton background under each peak properly.

11.3.2.2 Subtract the net background adjusted for the sample count time for each region of interest. To adjust the background measured for each region of interest used to measure the radium isotopes, multiply each region's count rate (cpm) obtained from the background measurement by the number of minutes the sample was counted. The software or calculation spreadsheet must then subtract this net background activity from the net counts in each photopeak's region of interest that is above the Compton background in the sample spectra to obtain the final net counts used in calculating the activity and uncertainty for the samples.

12.0 Data Analysis and Calculations

12.1 Sample activity concentration, the combined standard uncertainty of measurements of sample activity concentration made using this method, and method sensitivity are determined using the equations given below.

12.2 Calculate the concentration, A_S of Ra-228 and Ra-226 in picocuries per liter (pCi/L) as follows:

Assumptions:

- The detector is calibrated with a prepared radium source, not a mixed-gamma source.
- There is negligible uncertainty associated with the calibration.
- The uncertainties of times, volumes, and masses are negligible.
- There is negligible variability in replicate determinations of the carrier mass.
- There is negligible variability in the ratio of the radium and barium recoveries.

Given these assumptions, the only significant sources of uncertainty are counting statistics and the determination of net photopeak areas in the gamma-ray spectrum.

For both Ra-228 and Ra-226, the activity equation can be written as

$$A_S = \frac{W_1 \frac{R_1}{\varepsilon_1 F_1} + \cdots + W_n \frac{R_n}{\varepsilon_n F_n}}{2.22 \times V_S \times Y_S \times D_S} \tag{4}$$

where

A_S	is the sample activity concentration (pCi/L)
n	is the number of peaks used (typically $n = 2$)
R_i	(for $i = 1, 2, \ldots, n$) is the net count rate in counts per minute (min^{-1}) for peak i, corrected for baseline, background, and interferences
V_S	is the volume of the sample aliquant analyzed (L)
Y_S	is the chemical yield, or recovery, for the sample (fraction)
D_S	is the correction factor for decay/ingrowth (fraction)
ε_i	is the detection efficiency for peak i (fraction)
F_i	is the branching fraction for peak i (fraction)
W_i	is the weighting factor for peak i (fraction); $W_1 + W_2 + \cdots + W_n = 1$; e.g., W_i might be $\varepsilon_i F_i / (\varepsilon_1 F_1 + \cdots + \varepsilon_n F_n)$

Other unit conversions can be handled by including a constant factor in the denominator of the expression for A_S.

12.4 The equation for the combined standard uncertainty of A_S is shown below.

$$u_c(A_S) = \frac{\sqrt{W_1^2 \frac{u^2(R_1)}{\varepsilon_1^2 F_1^2} + \cdots + W_n^2 \frac{u^2(R_n)}{\varepsilon_n^2 F_n^2}}}{2.22 \times V_S \times Y_S \times D_S} \tag{5}$$

The values and uncertainties for R_i for $i = 1$ to n, should be provided by the gamma-analysis software. Note that the uncertainties of V_S, Y_S, D_S, and ε_i are assumed to be negligible, and the uncertainty of F_i does not affect the combined standard uncertainty of A_S when a radium source is used for efficiency calibration at each of the gamma-ray energies.

Any additional uncertainties for V_S, Y_S, D_S, or for the calibration standard or the yield obtained during the calibration can be included by adding terms to $u_c^2(A_S)$ that look like:

$$A_S^2 \frac{u^2(\text{Some quantity})}{(\text{Some quantity})^2}$$

12.5 Method Sensitivity

Since this method utilizes multiple photopeaks for quantitation, the sensitivity depends on the Compton baseline and on the background activity for each photopeak above the baseline. When Equation 4 is used for the activity concentration of a sample, the following equation may be used to estimate the SDWA detection limit:

$$\text{DL} = \frac{1.96^2}{2t_S} \sum_{i=1}^{n} \frac{W_i^2}{\varepsilon_i F_i} \left[1 + \sqrt{1 + \frac{4t_S^2}{1.96^2} \frac{\sum_{i=1}^{n} \frac{W_i^2 V (R_i)_{R_i=0}}{\varepsilon_i^2 F_i^2}}{\left(\sum_{i=1}^{n} \frac{W_i^2}{\varepsilon_i F_i} \right)^2}} \right] \times \frac{1}{2.22 \times V_S \times Y_S \times D_S} \tag{6}$$

where:

DL	is the SDWA detection limit, in picocuries per liter (pCi/L)
t_S	is the sample count time (min)
$V(R_i)_{R_i=0}$	is the variance of the observed net count rate, R_i, when the sample activity is zero

Each variance $V(R_i)_{R_i=0}$ may be estimated as follows:

$$V(R_i)_{R_i=0} = \frac{C_{S,Comp,i} + (C_{B,i} - C_{B,Comp,i}) \times t_S / t_B + u^2(C_{S,Comp,i})}{t_S^2} + \frac{C_{B,i} + u^2(C_{B,Comp,i})}{t_B^2} \quad (7)$$

where:

$C_{S,Comp,i}$	is the number of counts in sample peak i due to the Compton baseline of the sample spectrum
$u(C_{S,Comp,i})$	is the standard uncertainty of the estimated number of counts in sample peak i due to the Compton baseline (depends on the model used to estimate the baseline under the peak)
$C_{B,i}$	is the total count in the background peak (if any) for peak i, before correction for the Compton baseline of the background spectrum
$C_{B,Comp,i}$	is the number of counts in the background peak (if any) for sample peak i due to the Compton baseline of the background spectrum
$u(C_{B,Comp,i})$	is the standard uncertainty of the estimated number of counts in the background peak for sample peak i due to the Compton baseline
t_S	the sample count time (min)
t_B	is the background count time (min)

Note: If there is no background peak, omit the background terms in the equation above.

13.0 Method Performance

This method was validated through an inter-laboratory method validation study. There were 9 method ruggedness samples with known concentrations in these studies ($n = 9$). Table 13.1 below demonstrates the method has comparable or better performance when compared to EPA approved methods to measure these radioanalytes in drinking water.

Table 13.1. The accuracy and precision results derived from matrix spike and duplicated samples in the method ruggedness studies

Ra226	Percent Recovery	RPD	Ra228	Percent Recovery	RPD
Avg	99	7		101	6
Std. Dev.	7	6		9	6
Limit		19			18
Lower Limit	85			83	
Upper Limit	113			119	

One laboratory also conducted a study to document the equivalency of using lead as the carrier instead of barium. Table 13.2 below demonstrates the accuracy and precision for the 10 samples that were spiked with known amounts of the radioanalytes of interest.

Table 13.2. The accuracy and precision results derived from the matrix spike and duplicated samples in the lead carrier equivalency study.

	Percent			Percent	
Ra226	**Recovery**	**RPD**	**Ra228**	**Recovery**	**RPD**
Average	102	4		95	6
Std. Dev.	2	2		3	2

14.0 Pollution Prevention

14.1 The solvents used in this method pose little threat to the environment when recycled and managed properly.

14.2 Standards should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

15.0 Waste Management

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

15.2 Samples preserved with HCl or H_2SO_4 to pH < 2 are hazardous and must be neutralized before being disposed, or must be handled as hazardous waste.

15.3 For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel", and "Less is Better: Laboratory Chemical Management for Waste Reduction", both available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

15.4 Use of this method may result in the generation of mixed waste (MW). MW contains both hazardous waste (as defined by RCRA and its amendments) and radioactive waste (as defined by AEA and its amendments). It is jointly regulated by NRC or NRC's Agreement States and EPA or EPA's RCRA Authorized States. The fundamental and most comprehensive statutory definition is found in the Federal Facilities Compliance Act (FFCA) where Section 1004(41) was added to RCRA: "The term 'mixed waste' means waste that contains both hazardous waste and source, special nuclear, or byproduct material subject to the Atomic Energy Act of 1954." For more information on the handling and treatment of MW, please see http://www.epa.gov/radiation/mixed-waste/

16.0 References

16.1 "Methods for Chemical Analysis of Water and Wastes", 3rd Edition, Environmental Protection Agency, Environmental Monitoring Systems Laboratory-Cincinnati (EMSL-Ci), Cincinnati, Ohio 45268, EPA-600/4-79-020, Method 413.1, (1983).

16.2 "Standard Methods for the Examination of Water and Wastewater", 18th Edition, American Public Health Association, 1015 Fifteenth Street, NW, Washington, D.C. 20005, Method 5520B and Method 5520F, (1992).

16.3 40 CFR 136, Appendix A, Methods 1624 and 1625.

16.4 "Carcinogens - Working With Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

16.5 "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976).

16.6 "Safety in Academic Chemistry Laboratories," American Chemical Society, Committee on Chemical Safety, 3rd Edition, 1979.

16.7 "Standard Practices for Sampling Water," ASTM Annual Book of Standards, Part 31, D3370-76, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103-1187, 1980.

16.8 "Handbook of Analytical Quality Control in Water and Wastewater Laboratories," USEPA, EMSL-Ci, Cincinnati, OH 45268, EPA-600/4-79-019, March 1979.

16.9 "Method Validation Report: A Method for the Determination of Radium-226 and Radium 228 in Drinking Water by Gamma-ray Spectrometry Using HPGe and Ge(Li) Detectors." Available from the Sample Control Center, 6101 Stevenson Avenue, Alexandria, VA 22304.

16.10 Johnson, J.O. Determination of Radium-228 in Natural Waters. Radiochemical Analysis of Water, Geological Survey Water - Supply Paper 1696-G., U.S. Govt. Printing Office, Washington, DC (1971).

16.11 Interim Radiochemical Methodology for Drinking Water: Report EPA-600/4-75-008, March 1976.

16.12 Michel, J., Moore, W. S. and King, P. T. (1981) Gamma-ray spectrometry for determination of ^{228}Ra and ^{226}Ra in natural waters. Anal. Chem. 53, 1885-1889.

16.13 King, P. T., Michel, J. and Moore, W. S. (1982) Ground water geochemistry of ^{228}Ra, ^{226}Ra and ^{222}Rn. Geochimica et Cosmochimica Acta 46, 1173-1182.

16.14 Krishnaswami, S., Graustein, W. C. and Turekian, K. K. (1982) Radium, thorium and radioactive lead isotopes in groundwaters: application to the in situ determination of adsorption-desorption rate constants and retardation factors. Water Resources Research. 18, no.6, 1663–1675.

16.15 Moore, W. S. (1984) Radium isotope measurements using germanium detectors. Nuclear Instruments and Methods in Physics Research 223, 407–411.

16.16 Kahn, B. (1989) Screening Method for Radium-228 in Drinking Water, Assistance ID No. CR-813-630-01, submitted March 1989 to the EPA

16.17 Kahn, B., Rosson, R. and Cantrell, J. (1989) Determination of radium in ground water by gamma-ray spectral analysis. Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy abstract 239.

16.18 Kahn, B., Rosson, R. and Cantrell, J. (1990) Analysis of ^{228}Ra and ^{226}Ra in public water supplies by a γ-ray spectrometer. Health Physics. 59, 125–131.

16.19 American Society for Testing and Materials (ASTM). 1994. Standard Specification for Laboratory Glass Volumetric Flasks, E 288. ASTM, West Conshohocken, PA.

16.20 American Society for Testing and Materials (ASTM). 1995. Standard Specification for Glass Volumetric (Transfer) Pipets, E 969. ASTM, West Conshohocken, PA.

16.21 Reyss, J. L., Schmidt, S., Legeleux, F. and Bonte, P. (1995) Large low background well-type detectors for measurements of environmental radioactivity. Nuclear Instruments and Methods in Physics Research 357, 391–397.

16.22 Schmidt, S. and Reyss, J. L., (1996) Radium as internal tracer of Mediterranean outflow water. Journal of Geophysical Research, 101, no. C2, 3589-3596.

16.23 Hakam, O. K., Choukri, A., Moutia, Z., Chouak, A., Cherkaoui, R., Reyss, J.L. and Lferde, M. (2000) Activities and activity ratios of U and Ra radioisotopes in drinking water wells, springs and tap water samples in Morocco. Radiochim. Acta 88, 55-60.

16.24 American Society for Testing and Materials (ASTM). 2000. Standard Practice for Calibration of Laboratory Volumetric Glassware, E 542. ASTM, West Conshohocken, PA.

16.25 Luo, S., Ku, T., Roback, R., Murrell, M. and McLing T. L. (2000) In-situ radionuclide transport and preferential groundwater flows at INEEL (Idaho): decay-series disequilibrium studies. Geochimica et Cosmochimica Acta 64, 867–881.

16.26 Hakam, O. K., Choukri, A., Moutia, Z., Chouak, A., Cherkaoui, R., Reyss, J.L. and Lferde, M. (2001) Uranium and radium in groundwater and surface water samples in Morocco. Radiation Physics and Chemistry 61, 653–654.

16.27 Rosson, R., Kahn, B., Lahr, J. and Crowe, D. (2001) Measurement of ^{228}Ra and ^{226}Ra by γ-ray spectrometer in drinking water (abstract). 47th Annual Radiochemical Measurements Conference.

16.28 7500-Ra224 E. Gamma-ray spectroscopy method. (submitted) Standard Methods for the Examination of Water and Wastewater (21st Edition). Published by the American Public Health Association, the American Water Works Association and the Water Environment Federation

16.29 American Society for Testing and Materials (ASTM). 1999. Standard Specification for Reagent Water, D1193-99. ASTM, West Conshohocken, PA

17.0 Tables

Table 17.1. Acceptance Criteria for Performance Tests

Acceptance Criterion	Section	Limit (%)
Initial precision and recovery	9.2.2	
Ra-226 Precision (s)	9.2.2.2	12
Ra-226 Recovery (X)	9.2.2.2	76–125
Ra-228 Precision (s)	9.2.2.2	10
Ra-228 Recovery (X)	9.2.2.2	77–115
Matrix spike/matrix spike duplicate	9.3	
Ra-226 Recovery	9.3.4	85-113
Ra-226 RPD	9.3.5	12
Ra-228 Recovery	9.3.4	84-118
Ra-228 RPD	9.3.5	18
Ongoing precision and recovery	9.6	
Ra-226 Recovery	9.6	76–125
Ra-228 Recovery	9.6	77–115

Table 17.2: Sample Handling, Preservation, and Instrumentation

Parameter	Preservative[1]	Container[2]	Maximum Holding Time[3]
Radium-226	Conc. HCl or HNO_3 to pH <2	P or G	6 mo
Radium-228	Conc. HCl or HNO_3 to pH <2	P or G	6 mo

[1]It is recommended that the preservative be added to the sample at the time of collection. However, if the sample has to be shipped to a laboratory or storage area, acidification of the sample (in its original container) may be delayed for a period not to exceed 5 days. A minimum of 16 hours must elapse between acidification and analysis.
[2]P = Plastic, hard or soft; G = Glass, hard or soft.
[3]Holding time is defined as the period from time of sampling to time of analysis. In all cases, samples should be analyzed as soon after collection as possible. If a composite sample is prepared, a holding time cannot exceed 12 months.

Table 17.3. Ingrowth Factors for Short –lived Radium-226 Progeny y

	% Ingrowth		% Ingrowth		% Ingrowth
Day1	0.165	Day2	0.304	Day3	0.419
Day4	0.515	Day5	0.595	Day6	0.662
Day7	0.718	Day8	0.765	Day9	0.804
Day10	0.836	Day11	0.863	Day12	0.886
Day13	0.905	Day14	0.920	Day15	0.933
Day16	0.944	Day17	0.954	Day18	0.961
Day19	0.968	Day20	0.973	Day21	0.977
Day22	0.981	Day23	0.984	Day24	0.987
Day25	0.989	Day26	0.991	Day27	0.992

18.0 Glossary of Definitions and Purposes

The definitions and purposes are specific to this method but have been conformed to common usage as much as possible.

18.1 Units of weight and measure and their abbreviations

18.1.1 Symbols

°C	degrees Celsius
<	less than
%	percent
±	plus or minus

18.1.2 Alphabetical characters

g	gram
h	hour
L	liter
mg	milligram
mg/L	milligram per liter
mg/mL	milligram per milliliter
mL	milliliter
No.	number

18.2 Definitions, acronyms, and abbreviations

18.2.1 Analyte: The Ra-226 or Ra-228 tested for by this method.

18.2.2 Analytical batch: The set of samples extracted at the same time, to a maximum of 10 samples. Each analytical batch of 10 or fewer samples must be accompanied by a laboratory blank (Section 9.4), an ongoing precision and recovery sample (OPR, Section 9.6), and a matrix spike and matrix spike duplicate (MS/MSD, Section 9.3), resulting in a minimum of five analyses (1 sample, 1 blank, 1 OPR, 1 MS, and 1 MSD) and a maximum of 14 analyses (10 samples, 1 blank, 1 OPR, 1 MS, and 1 MSD) in the batch. If greater than 10 samples are to be extracted at one time, the samples must be separated into analytical batches of 10 or fewer samples.

18.2.3 Field blank: An aliquant of reagent water that is placed in a sample container in the laboratory or in the field and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.

18.2.4 IPR: See initial precision and recovery.

18.2.5 Initial precision and recovery (IPR): Four aliquants of the diluted PAR analyzed to establish the ability to generate acceptable precision and accuracy. An IPR is performed the first time this method is used and any time the method or instrumentation is modified.

18.2.6 Laboratory blank (method blank): An aliquant of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The laboratory blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

18.2.7 Laboratory control sample (LCS): See Ongoing precision and recovery standard (OPR).

18.2.8 Matrix spike (MS) and matrix spike duplicate (MSD): Aliquants of an environmental sample to which known quantities of the analytes are added in the laboratory. The MS and MSD are prepared and/or analyzed exactly like a

field sample. Their purpose is to quantify any additional bias and imprecision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquant and the measured values in the MS and MSD corrected for background concentrations.

18.2.9 May: This action, activity, or procedural step is neither required nor prohibited.

18.2.10 May not: This action, activity, or procedural step is prohibited.

18.2.11 Method Detection Limit: The lowest level at which an analyte can be detected with 99 percent confidence that the analyte concentration is greater than zero.

18.2.12 Minimum Level (ML): The lowest level at which the entire analytical system gives a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

18.2.13 Must: This action, activity, or procedural step is required.

18.2.14 Ongoing precision and recovery standard (OPR, also called a laboratory control sample): A laboratory blank spiked with known quantities of analytes. The OPR is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and accuracy.

18.2.15 OPR: See Ongoing precision and recovery standard.

18.2.16 PAR: See Precision and recovery standard.

18.2.17 Precision and recovery standard: Secondary standard that is diluted and spiked to form the IPR and OPR.

18.2.18 Quality control sample (QCS): A sample containing analytes of interest at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from standards obtained from a different source than the calibration standards. The purpose is to check laboratory performance using test materials that have been prepared independently from the normal preparation process.

18.2.19 Reagent water: Water demonstrated to be free from Ra-226, Ra-228 and potentially interfering substances at or above the Minimum Level of this method.

18.2.20 Should: This action, activity, or procedural step is suggested but not required.

18.2.21 Stock solution: A solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

Experiment 8*

Determination of Radium-226 and Radium-228 in Drinking Water

Objective

To measure the naturally-occurring radium isotopes ^{226}Ra and ^{228}Ra in drinking water.

Introduction

One important parameter in determining the quality of drinking water is the measurement of its radioactivity level. The two main radium isotopes of concern are ^{226}Ra, a progeny of naturally-occurring ^{238}U, and ^{228}Ra, a progeny of naturally-occurring ^{232}Th. The decay series for these natural radionuclides, as well as ^{235}U, are given in Appendices 2–4.

Earlier methods used in the analysis of radium isotopes in water required labor-intensive radiochemical separations and subsequent measurement of alpha particles for ^{226}Ra and beta particles for ^{228}Ra. The method used in this experiment applies simpler gamma-ray spectral analysis of the progeny of both ^{226}Ra and ^{228}Ra.

The analysis, described in Part 8A, begins with the co-precipitation of ^{226}Ra and ^{228}Ra on barium sulfate (K_{sp} = 1.0 x 10^{-10}). The precipitate is collected on filter paper and stored, to await the ingrowth of radioactive progeny. The ^{222}Rn daughter of ^{226}Ra is strongly retained in the barium sulfate precipitate, together with its short-lived progeny that emit gamma rays. The ^{228}Ac daughter of ^{228}Ra that emits gamma rays co-precipitates together with its parent. By counting a major gamma ray from ^{214}Pb (351.9 keV) and one from ^{214}Bi (609.3 keV), the activity of ^{226}Ra is determined. By counting two major gamma rays emitted by ^{228}Ac (338.3 and 911.2 keV), the activity of ^{228}Ra is determined. Measurement of two gamma rays per radium parent is recommended to balance the lesser detection efficiency with use of only one gamma ray each, and the greater potential for interferences with the additional (more than 2) gamma rays that are emitted.

---

*Prepared by Robert Rosson, Environmental Radiation Center, EOSL, GTRI, Georgia Institute of Technology, Atlanta GA 30332–0841

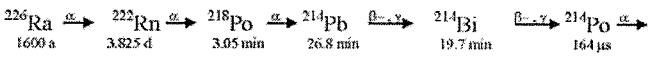


Figure 8.1 Radium-226 and direct progeny.

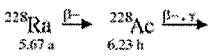


Figure 8.2 Radium-228 and direct progeny.

Figures 8.1 and 8.2 show the short-lived radioactive decay chains for ^{226}Ra and ^{228}Ra, respectively, to illustrate the relationship of the progeny to the two radium isotopes. Long-lived radionuclides continue both the chains.

For ^{226}Ra, 26 days are needed (based on 7 half lives of the longest-lived progeny in the chain, ^{222}Rn) to reach 99% of radioactive equilibrium of the progeny. If less time is to be allowed for the ingrowth of ^{222}Rn, then the fractional ingrowth must be calculated to obtain the amount of ^{226}Ra in the sample. For this calculation, the ingrowth factor is $(1-e^{-\lambda t})$ where λ is the decay constant ($\lambda = 0.693/t_{1/2}$) for ^{222}Rn. The ingrowth calculation is illustrated in Example 1.

Example 1

Problem: A purified radium sample is counted for gamma rays, 5.2 days after the chemical separation of barium sulfate from a water sample. (5.2 days is the interval from the separation time to the mid-time of the counting period). What fraction of the activity of ^{226}Ra is observed in the gamma ray count?

Solution: The half life of ^{222}Rn is $t_{1/2}$= 3.825 days. The equation for the fraction of equilibrium activity is:

$$1 - e^{-\lambda_{226} t}$$

Insert the appropriate values:

$$\lambda_{226} = \frac{0.693}{3.835} = 0.181\,\text{days}^{-1}$$

$$t = 5.2\ \text{days}$$

$$1 - e^{-\lambda_{226} t} = 1 - e^{-0.9421} = 1 - 0.39 = 0.61$$

The activity observed at 5.2 days is 61% of saturation activity. The value observed at the 5.2 day count time is divided by 0.61 to obtain value of the saturation activity.

The case of ^{228}Ra is simpler than that in Example 1. Although the half life of ^{228}Ac requires a 2-day interval to exceed 99% of equilibrium, no delay is needed because ^{228}Ac also is co-precipitated with barium sulfate, so that initial radioactive equilibrium within the precipitate remains undisturbed.

Hence, the sample can be counted immediately for its ^{228}Ra content with the Ge detector and gamma-ray spectrometer system. The count must be delayed only for ingrowth of the ^{226}Ra progeny. A screening measurement of gross alpha activity prescribed by EPA in its drinking-water regulations specifies

that a gross alpha-particle activity of 5 pCi/L (0.2 Bq/L) or less eliminates the need for ^{226}Ra analysis, and thus, the need for delayed counting.

Some water samples also contain 3.66-d ^{224}Ra, a progeny of ^{228}Ac and ^{228}Th. If the sample is measured within about one week of collection by gamma-ray spectrometer, the characteristic gamma rays of ^{224}Ra (at low intensity) and of its progeny ^{212}Pb and ^{208}Tl (at higher intensity) can be detected. Storing the water sample for several weeks before processing will remove ^{224}Ra by radioactive decay.

A reagent blank is processed in Part 8B of this experiment to resolve the problem of contamination due to airborne ^{222}Rn and its progeny. The special background problem encountered with measuring progeny of ^{226}Ra is that one of them – ^{222}Rn – is a gas that emanates from the ground and building materials such as concrete and brick, accompanies the air in the laboratory and the counting room, and can be retained in the barium sulfate precipitate and its filter paper. The concentration of ^{222}Rn and its short-lived progeny in air fluctuates with meteorological conditions and room ventilation, so that the background count rate in the spectral analysis regions of interest also can vary. To resolve this problem, either the contamination due to ^{222}Rn progeny must be maintained sufficiently low that its fluctuation does not measurably affect the count rate, or the background must be monitored for each batch of samples.

In Part 8C, the barium carrier is prepared and a standard source of ^{226}Ra and ^{228}Ra is prepared and counted to calibrate the Ge detector for this radium analysis. The counting efficiency for three of the four characteristic gamma rays that are used to determine the activity of the two radium isotopes can be derived from a curve of efficiency *vs.* energy of the type prepared in Experiment 2. The efficiency for the 0.6093-MeV gamma ray, however, lies below this curve because of a complication associated with two gamma rays that are emitted simultaneously with good efficiency, in this case, numerous more energetic gamma rays of ^{214}Bi. The counting efficiency of this gamma ray must be determined for the specific Ge detector dimensions and sample location.

Safety Reminder

- Follow the usual safety procedures when working in a radiological laboratory.
- Caution should be exercised when preparing and working with corrosive mineral acids.
- All liquids and solids are to be properly disposed according to laboratory rules and protocol.

Equipment

- 10-mL and 1,000 mL graduated cylinders
- Borosilicate beaker, 1- 2-, or 4-L
- Beakers, 100 mL
- Stirring rods, glass
- Pipette, 5 mL

- Pipetter capable of measuring tenths of mL
- Heated magnetic stirrer and stir bar
- Analytical balance (capable of weighing to nearest 0.01 mg)
- Filtering apparatus
- Filter circles (Whatman 42, 2.5 cm diameter or suitable size for filtering apparatus)
- Ring and Disk mount
- Mylar film cover
- Vacuum pump
- Reagent bottles
- Sintered-glass crucible, fine porosity
- Drying oven
- Plastic squirt bottle for deionized water

Note: All glassware for the experiment should be acid-washed and rinsed with deionized water before use.

Reagents

- ^{226}Ra standard solution, diluted to concentration of about 40 Bq per mL, in 0.01 N HNO_3
- ^{228}Ra standard solution, diluted to concentration of about 40 Bq per mL, in 0.01 N HNO_3
- Concentrated HNO_3
- Concentrated HCl
- Concentrated H_2SO_4
- Barium chloride: Reagent grade $BaCl_2.2H_2O$
- Barium carrier, standardized, 9 mg Ba^{2+}/mL: Dissolve 16.01 g of $BaCl_2.2H_2O$ in deionized water, add 5 mL of concentrated nitric acid, and dilute to 1 L with deionized water. (See **Barium Carrier Standardization** at end of Part 8C.)
- Sulfuric acid, 18 N: Cautiously add 500 mL of concentrated sulfuric acid to 400 mL of deionized water and dilute to 1 L with deionized water. *Note: The reaction of concentrated sulfuric acid with water is an extremely exothermic one. Add concentrated sulfuric acid to water in small quantities, with stirring.*
- Sulfuric acid, 0.01 N: Add 0.55 mL of 18 N H_2SO_4 to 100 mL deionized water and dilute to 1 L.
- Ethanol, 95%
- Diethyl ether

8A. Determination of Radium in Drinking Water

Procedure

Step 1. Measure the volume of preserved drinking water in a large graduated cylinder and record the volume to the nearest 1 mL. The sample should have been preserved with 4 mL of concentrated HNO3 per gallon (3.7 L) of drinking water or enough concentrated HNO_3 to make the pH of the water < 2.

Transfer to a beaker. *The instructor will specify the quantity of water in the sample.*

Step 2. Add 10 mL of concentrated HCl for every liter of water used and mix thoroughly.

Step 3. Accurately pipette 5.0 mL of barium carrier (9 mg/mL) into the sample. Stir and heat to boiling.

Step 4. Precipitate barium sulfate by adding 10 mL of 18 N H_2SO_4 in a fine stream while stirring. Record the date and time of precipitation. Cool 30 minutes in an ice bath or allow overnight settling in covered beaker.

Date and time of $BaSO_4$ precipitation: _____

Note: The following steps describe a specific method of filtering, weighing and mounting the sample. The instructor may provide alternate instructions for preparing the barium sulfate source appropriate for the available counting facilities.

Step 5. Filter the solution that contains the $BaSO_4$ through a tared filter. One approach is to let the precipitate settle and then decant carefully approximately 800 mL of a 1-L sample; slurry the precipitate in the remaining water, pour it through the filter; and wash any remaining precipitate from the beaker to the filter with a jet of deionized water. *Avoid pulling excess air through the filter because airborne radon progeny will add to the sample counting results (see Part 8B).*

Step 6. Wash and dry the precipitate on the filter with 10 mL of ethanol, followed by 10 mL of diethyl ether. Turn off the suction as the last of the diethyl ether passes through the filter.

Step 7. Remove the dried filter with the precipitate. Weigh the tared filter on a tared planchet to the nearest 0.1 mg. Record the weight in Data Table 8.1

Step 8. Mount the precipitate in a holder such as a ring and disk with Mylar cover. Label the sample according to counting room protocol.

Step 9. Count immediately for 60,000 s with a Ge detector plus gamma-ray spectrometer to observe the gamma rays emitted by the ^{228}Ra daughter in the sample if these results are needed promptly. Count after 2 – 4 weeks to permit ingrowth of the ^{226}Ra progeny and determine the levels of both ^{226}Ra and ^{228}Ra. Record mid-time of counting. Record net count rates in energy regions of interest in Data Table 8.2 and 8.3.

Dates and mid-times of counting: _____

Chemical Yield Calculation

Subtract the tared filter paper plus planchet weight from the combined weight of the filter, planchet, and precipitate to determine the net weight of the $BaSO_4$ precipitate. Enter result in Data Table 8.1 Divide this net weight of the precipitate by the theoretical weight of the precipitate based on the amount of

standardized barium carrier that is used in the precipitate. This is the chemical yield (Y_s) for the sample precipitate.

Data Table 8.1 Chemical yield

	Mass
Filter Paper + Precipitate + planchet	
Filter Paper + planchet	
Barium Carrier (as $BaSO_4$)	

$$\frac{\textit{Final mass of barium sulfate}}{\textit{Initial mass of barium sulfate}} = \textit{chemical yield} \qquad (8.1)$$

Chemical Yield = _____

Counting

After the selected ingrowth period, record the time and count the sample according to the counting procedures. The count time may be adjusted if the radium concentration is higher than usual or the detector counting efficiency is unusually high or low.

Ingrowth interval: _____

Treatment of Gamma-Ray Counting Data

Radium-226 Concentration Calculation

Determine the amount of ^{226}Ra according to the following equation for the 351.9 keV gamma-ray of the progeny ^{214}Pb and the 609.3 keV gamma-ray of the progeny ^{214}Bi, respectively.

$$A_s = \left[\frac{1}{(0.037)VY_sD_s\varepsilon}\right]\left(\frac{R}{F_i}\right) \qquad (8.2)$$

Where

A_s = the concentration of ^{226}Ra in pCi/L,

0.037 = conversion factor from disintegrations per second to picocuries (pCi) [0.037 dps = 1 pCi],

Y_s = chemical yield determined for the sample,

D_s = ingrowth factor $(1 - e^{-\lambda t})$, where $\lambda = 0.693/t_{1/2}$; t = time interval in d between the separation of the radium from the water and the midpoint of the counting time, and $t_{1/2}$ = half life of ^{222}Rn of 3.82 d,

R = net counts per s for the gamma-ray under consideration (background and Compton contributions have been subtracted; the uncertainty or error reported for that gamma ray should be noted),

F_i = branching ratio for gamma-ray under consideration; see Data Table 8.2 for value,

ε = counting efficiency of specific gamma ray; see Part 8.C for measurement, and
V = sample volume, L.

Record all information in DataTable 8.2 Based on the values calculated for each gamma-ray and their respective uncertainties, calculate a weighted average for the two. See section on **Weighted Average Calculations** in Appendix 6. Report the value as pCi or Bq ^{226}Ra per L water with its uncertainty.

Data Table 8.2 Activity of ^{226}Ra

^{226}Ra	351.9 keVγ	609.3 keVγ
Sample volume (V)		
Chemical Yield Fraction (Y)		
Ingrowth factor (D)		
Net gamma ray count rate (R)		
Branching ratio (F_i)	0.358	0.448
Counting efficiency (ε)		
Activity ^{226}Ra (pCi/L ± σ)		

Activity ^{226}Ra in pCi/L (weighted average)_____

Radium-228 Concentration Calculation

Determine the amount of ^{228}Ra according to the above equation, but for the 338.3 keV and 911.2 keV gamma-rays of the progeny ^{228}Ac. The following items are different from the above equation for ^{226}Ra:

D_s refers to the ^{228}Ac half-life of 6.15 h, but parent and daughter are in equilibrium (D_s = 1.00) immediately because both are co-precipitated with barium sulfate.

F_i refers to the branching ratios of the two characteristic gamma rays of ^{228}Ac that are shown in Data Table 8.3

Record the data for this set of calculations in Data Table 8.3 Based on the values calculated for each gamma-ray and their respective uncertainties, calculate a weighted average for the two. See section on **Weighted Average Calculations** in Appendix 6. Report the value as pCi or Bq ^{228}Ra per L water with its uncertainty.

Data Table 8.3 Activity of ^{228}Ra

^{228}Ra	338.3 keVγ	911.2 keVγ
Sample volume (V)		
Chemical Yield Fraction (Y)		
Ingrowth factor (D)		
Net gamma ray count rate (R)		
Branching ratio (F_i)	0.113	0.266
Counting efficiency (ε)		
Activity ^{228}Ra (pCi/L ± σ)		

Activity ^{228}Ra in pCi/L (weighted average)_____

8B. Preparation of a Reagent Blank and Testing for Airborne Radon and Progeny

Procedure

Note: If both the reagent blank and testing for airborne radon progeny are to be done, perform the two samples in parallel. Make certain that glassware could not have accumulated radon progeny from air while standing in the open.

Step 1. *Reagent blank.* Measure a 1-liter volume of deionized water. Add 1 mL of concentrated HNO_3 to the sample. Pour the measured volume into a clean borosilicate beaker large enough to contain it without spilling, e.g., 2-L volume.

Step 2. Add 10 mL of concentrated HCl to the deionized water and mix thoroughly.

Step 3. Accurately pipette 5.0 mL of barium carrier (9 mg/mL)into the sample. Stir and heat to boiling.

Step 5. Precipitate barium sulfate by adding slowly 10 mL of 18 N H_2SO_4 in a fine stream with stirring. Record date and time of separation of radon daughter plus progeny from radium parent. Cool 30 minutes in an ice bath or allow to digest overnight covered..

Note: The following steps describe a specific method of filtering, weighing and mounting the sample. The instructor may provide alternate instructions for preparing the barium sulfate source appropriate for the available counting facilities.

Date and time of radium separation:_____

Step 6. Place a tared filter of the type and dimensions used in Procedure 8A in the filter funnel apparatus that is attached to a vacuum source.

Step 7a. *For reagent blank.* Filter the $BaSO_4$ solution on the tared filter paper. Keep filtration time to a minimum and measure the total time that the air is drawn through the filter. Wash the precipitate that remains in the beaker to the filter by rinsing the beaker with a jet of deionized water. Wash and dry the precipitate on the filter with 10 mL of ethanol, followed by 10 mL of diethyl ether. Turn off the suction when the final amount of diethyl ether has passed through the filter.

OR

Step 7b. For *detection of airborne radon progeny.* Filter a reagent blank solution that contains the $BaSO_4$ on the tared filter paper. Wash the precipitate that remains in the beaker to the filter by rinsing the beaker with a jet of deionized water. Wash and dry the precipitate on the filter with 10 mL of ethanol, followed by 10 mL of diethyl ether. Draw air through the sample for a measured time of 30 minutes to 1 hour to collect airborne radon and

Data Table 8.4 Chemical yield of blank and airborne sample

	Blank	Airborne Sample
Filter Paper + Precipitate, mg		
Filter Paper, mg		
Barium Carrier (as precip. $BaSO_4$), mg		
Chemical Yield		

daughters. Record date, time of collection of radon progeny from air, and collection period.

Date, time, and period of collection of radon progeny from air: _____

Step 8. Remove the filter with the precipitate. Weigh the tared filter on a tared planchet the nearest 0.1 mg. Record the weight in Table 8.4

Step 9. Mount the precipitate on a holder such as a ring and disk, and cover with Mylar film. Label the sample according to counting room protocol.

Step 10. Count the gamma rays emitted by the sample with a Ge detector plus spectrometer after the same time interval as in Procedure 8A. The airborne radioactivity sample should be counted as soon as possible after sample collection, with data recorded in Data Table 8.5 Repeat counting after selected intervals and record in Data Table 8.6, as indicated below. Determine the chemical yield as described in Procedure 8A, based on the information recorded in Data Table 8.4

Counting

Reagent Blank. Inspect the gamma-ray spectrum carefully to determine if any of the gamma-rays from radium-226 are present. If so, record results in Data Table 8.5 Determine the amount according to the process described in Part 8A.

Activity ^{226}Ra in pCi/L (weighted averages): _____

Airborne Radon Progeny. Scheme 1. Count the sample immediately on the germanium detector, recording the time interval from separation to filtration Record in Data Table 8.5 Then count again in one week, followed by a third

Data Table 8.5 Activity of ^{226}Ra in blank and airborne sample

	351.9 keV	609.3 keV	351.9 keV	609.3 keV
Sample volume (V)	Blank		Airborne Sample	
Chemical Yield Fraction (Y)				
Ingrowth factor (D)				
Net gamma ray count rate (R)				
Branching ratio (F_i)	0.358	0.448	0.358	0.448
Counting efficiency (ε)				
Activity ^{226}Ra (pCi/L $\pm$ σ)				

Data Table 8.6 Gamma-ray decay study of radionuclides on filters

Gamma-ray energy and net count rate interval, d	Count 1		Count 2		Count 3	
	351.9	609.3	351.9	609.3	351.9	609.3

Data Table 8.7 Alpha- and beta-particle decay study

Interval, d	Gross α (cps)	Bkgd. α (cps)	Net α (cps)	Gross β(cps)	Bkgd. β(cps)	Net β(cps)

count in two weeks after sample collection. Be sure to compare the spectrum of the sample to a detector background spectrum counted the same length of time. Record results in Data Table 8.6. Identify the radionuclides by gamma ray spectrometry.

Scheme 2. Count the sample immediately with an α and β counter (e.g., the proportional counter) for 200 minutes. Repeat the count each day for 14 days or until the count rate equals or nearly equals the background. Obtain background counts for both alpha-particle and beta-particle counting modes. Subtract respective backgrounds for each count period and record in Data Table 8.7

Plot data of alpha-particle and beta-particle net count rates (on log scale) on the same graph versus time (linear scale) in days.

8C. Preparation of ^{226}Ra and ^{228}Ra Standard and Barium Carrier

Procedure

Preparation and counting of ^{226}Ra and ^{228}Ra standards for calibration of Ring and Disk source *(in triplicate)*

Step 1. Pipette exactly 5 mL of barium carrier into 100-mL beaker that contains 20 ml of deionized water. Add 5 drops of concentrated HCl. Pipette 1 ml of ^{226}Ra standard solution and also pipette 1 mL of ^{228}Ra standard solution into the beaker. Stir well.

Data Table 8.8 Radium count rate

	^{226}Ra		^{228}Ra	
Energy (keV)	351.9 γ	609.3 γ	338.3 γ	911.2 γ
Decay fraction	0.358	0.448	0.113	0.266
Yield (fraction)				
Activity (dps)				
Gross count rate (cps)				
Net count rate (cps)				
Count rate, ingrowth corrected (cps)				
Counting efficiency				

Step 2. Heat the solution to boiling and add 20 ml of 18 N H_2SO_4 in a steady stream with stirring to precipitate $BaSO_4$ with radium standards. Digest while boiling for 10 minutes. Let solution cool.

Date and time of precipitation: _____

Step 3. Pour slurry through tared filter circle in filtering apparatus. Rinse beaker with four 5-mL portions of 0.01 N H_2SO_4 onto filter. Wash and dry filter and precipitate with 10 mL of ethanol and then with 10 ml of diethyl ether.

Step 4. Transfer filter to tared planchet and weigh. Subtract tared weights to calculate weight of $BaSO_4$ and the yield of $BaSO_4$ relative to the pipetted amount. Record yield in Data Table 8.8 Prepare filter on a holder such as a ring and disk with Mylar film cover. Store for counting.

Step 5. After interval of about 4 weeks since $BaSO_4$ precipitation, count filter in holder with Ge detector and spectrometer for at least 3,000 s. Make certain that location of holder relative to the detector is identical for this calibration measurement and all sample measurements.

Step 6. Record the gross count rates of all four characteristic peaks in Data Table 8.8 Calculate the net count rate for each peak. Use equation 8.2 (given in Procedure 8A) to calculate the counting efficiency, ε, for each of the four gamma rays; this is based on the activity, A_s, of each of the two standard solutions in the pipetted solution volume, V (i.e., 1 mL). The ingrowth factor, D_s, is 1.00 for ^{228}Ra and 0.99 for ^{226}Ra when the interval between radium precipitation and counting is 26 days. Calculate the average counting efficiency and standard deviation.

Barium carrier standardization *(in triplicate)*

Step 1. Pipette exactly 5.0 mL of carrier into a clean 100-mL beaker that contains 20 mL of deionized water. Add 5 drops of concentrated HCl. Heat the solution to boiling and add 20 mL of 18 N H_2SO_4 in a steady stream with stirring. Digest the sample on the hot plate for 10 minutes. Remove the beaker from the hot plate and let the solution cool to room temperature.

Step 2. Slurry the precipitate and filter into a clean, tared sintered-glass crucible of fine porosity. Rinse beaker with four 5-mL portions of 0.01 N H_2SO_4 and add to filter to ensure quantitative transfer of all of the precipitate to the crucible. Wash the precipitate twice with 20 mL of 0.01 N H_2SO_4.
Step 3. Remove the crucible from the filtering funnel and dry in the oven at 110°C for 2 hours.

Step 4. Place the crucible in a desiccator to cool. Weigh to constant weight. Record the weight for calculating the barium mass per mL. Report the average standardized barium in mg Ba^{2+}/mL and as $BaSO_4$/mL (to the nearest 0.1 mg) and label bottle (see Experiment 5). The spread in the values should be less than 1%.

Net weight of $BaSO_4$: (1)_____; (2)_____ ;(3)_____; (average)_____

Questions

1. If a sample contains 0.56 pCi ^{226}Ra per L, (a) calculate the mg/L of ^{226}Ra in the water. (b) Calculate the mg/L of natural uranium that would be in the water if the ^{226}Ra is in radioactive equilibrium with its parent ^{238}U.
2. List the assumption(s) associated with the reported chemical yield for the recovery of radium by its co-precipitation on $BaSO_4$. Design an experiment to test assumptions.
3. If the chemical yield for several samples is in excess of 100%, offer plausible explanations that would give rise to this observation. How would you correct or compensate for this observation?
4. Three different laboratories conduct an experiment to determine the amount of airborne radioactivity on $BaSO_4$. Laboratory A finds no activity; B observes both alpha and beta activity that decay with a half life of several days; C observes alpha and beta activity that increase with time. Explain their disparate findings.
5. If airborne activity is a serious and troublesome problem for a laboratory, suggest ways to eliminate or minimize it.
6. Calculate the amount of barium carrier that will remain in a 4-L sample, as described here. What percent barium is lost due to its solubility? Design an experiment to check this result. See the introduction for the solubility product value.

Source

Adapted from "Method for the Determination of Radium-228 and Radium-226 in Drinking Water by Gamma-ray Spectrometry Using HPGE or Ge(Li) Detectors", ERC, GTRI, Georgia Institute for Technology, Atlanta, GA, an Approved Test Procedure of the US EPA (see Federal Register, March 12, 2007, pp. 11,200–11,249).

Experiment 8*

Determination of Radium-226 and Radium-228 in Drinking Water

Objective

To measure the naturally-occurring radium isotopes ^{226}Ra and ^{228}Ra in drinking water.

Introduction

One important parameter in determining the quality of drinking water is the measurement of its radioactivity level. The two main radium isotopes of concern are ^{226}Ra, a progeny of naturally-occurring ^{238}U, and ^{228}Ra, a progeny of naturally-occurring ^{232}Th. The decay series for these natural radionuclides, as well as ^{235}U, are given in Appendices 2–4.

Earlier methods used in the analysis of radium isotopes in water required labor-intensive radiochemical separations and subsequent measurement of alpha particles for ^{226}Ra and beta particles for ^{228}Ra. The method used in this experiment applies simpler gamma-ray spectral analysis of the progeny of both ^{226}Ra and ^{228}Ra.

The analysis, described in Part 8A, begins with the co-precipitation of ^{226}Ra and ^{228}Ra on barium sulfate (K_{sp} = 1.0 x 10^{-10}). The precipitate is collected on filter paper and stored, to await the ingrowth of radioactive progeny. The ^{222}Rn daughter of ^{226}Ra is strongly retained in the barium sulfate precipitate, together with its short-lived progeny that emit gamma rays. The ^{228}Ac daughter of ^{228}Ra that emits gamma rays co-precipitates together with its parent. By counting a major gamma ray from ^{214}Pb (351.9 keV) and one from ^{214}Bi (609.3 keV), the activity of ^{226}Ra is determined. By counting two major gamma rays emitted by ^{228}Ac (338.3 and 911.2 keV), the activity of ^{228}Ra is determined. Measurement of two gamma rays per radium parent is recommended to balance the lesser detection efficiency with use of only one gamma ray each, and the greater potential for interferences with the additional (more than 2) gamma rays that are emitted.

---

*Prepared by Robert Rosson, Environmental Radiation Center, EOSL, GTRI, Georgia Institute of Technology, Atlanta GA 30332–0841

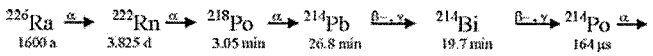


Figure 8.1 Radium-226 and direct progeny.

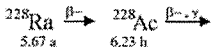


Figure 8.2 Radium-228 and direct progeny.

Figures 8.1 and 8.2 show the short-lived radioactive decay chains for ^{226}Ra and ^{228}Ra, respectively, to illustrate the relationship of the progeny to the two radium isotopes. Long-lived radionuclides continue both the chains.

For ^{226}Ra, 26 days are needed (based on 7 half lives of the longest-lived progeny in the chain, ^{222}Rn) to reach 99% of radioactive equilibrium of the progeny. If less time is to be allowed for the ingrowth of ^{222}Rn, then the fractional ingrowth must be calculated to obtain the amount of ^{226}Ra in the sample. For this calculation, the ingrowth factor is $(1-e^{-\lambda t})$ where λ is the decay constant ($\lambda = 0.693/t_{1/2}$) for ^{222}Rn. The ingrowth calculation is illustrated in Example 1.

Example 1

Problem: A purified radium sample is counted for gamma rays, 5.2 days after the chemical separation of barium sulfate from a water sample. (5.2 days is the interval from the separation time to the mid-time of the counting period). What fraction of the activity of ^{226}Ra is observed in the gamma ray count?

Solution: The half life of ^{222}Rn is $t_{1/2}$= 3.825 days. The equation for the fraction of equilibrium activity is:

$$1 - e^{-\lambda_{226} t}$$

Insert the appropriate values:

$$\lambda_{226} = \frac{0.693}{3.835} = 0.181\ \text{days}^{-1}$$

$$t = 5.2\ \text{days}$$

$$1 - e^{-\lambda_{226} t} = 1 - e^{-0.9421} = 1 - 0.39 = 0.61$$

The activity observed at 5.2 days is 61% of saturation activity. The value observed at the 5.2 day count time is divided by 0.61 to obtain value of the saturation activity.

The case of ^{228}Ra is simpler than that in Example 1. Although the half life of ^{228}Ac requires a 2-day interval to exceed 99% of equilibrium, no delay is needed because ^{228}Ac also is co-precipitated with barium sulfate, so that initial radioactive equilibrium within the precipitate remains undisturbed.

Hence, the sample can be counted immediately for its ^{228}Ra content with the Ge detector and gamma-ray spectrometer system. The count must be delayed only for ingrowth of the ^{226}Ra progeny. A screening measurement of gross alpha activity prescribed by EPA in its drinking-water regulations specifies

that a gross alpha-particle activity of 5 pCi/L (0.2 Bq/L) or less eliminates the need for ^{226}Ra analysis, and thus, the need for delayed counting.

Some water samples also contain 3.66-d ^{224}Ra, a progeny of ^{228}Ac and ^{228}Th. If the sample is measured within about one week of collection by gamma-ray spectrometer, the characteristic gamma rays of ^{224}Ra (at low intensity) and of its progeny ^{212}Pb and ^{208}Tl (at higher intensity) can be detected. Storing the water sample for several weeks before processing will remove ^{224}Ra by radioactive decay.

A reagent blank is processed in Part 8B of this experiment to resolve the problem of contamination due to airborne ^{222}Rn and its progeny. The special background problem encountered with measuring progeny of ^{226}Ra is that one of them – ^{222}Rn – is a gas that emanates from the ground and building materials such as concrete and brick, accompanies the air in the laboratory and the counting room, and can be retained in the barium sulfate precipitate and its filter paper. The concentration of ^{222}Rn and its short-lived progeny in air fluctuates with meteorological conditions and room ventilation, so that the background count rate in the spectral analysis regions of interest also can vary. To resolve this problem, either the contamination due to ^{222}Rn progeny must be maintained sufficiently low that its fluctuation does not measurably affect the count rate, or the background must be monitored for each batch of samples.

In Part 8C, the barium carrier is prepared and a standard source of ^{226}Ra and ^{228}Ra is prepared and counted to calibrate the Ge detector for this radium analysis. The counting efficiency for three of the four characteristic gamma rays that are used to determine the activity of the two radium isotopes can be derived from a curve of efficiency *vs.* energy of the type prepared in Experiment 2. The efficiency for the 0.6093-MeV gamma ray, however, lies below this curve because of a complication associated with two gamma rays that are emitted simultaneously with good efficiency, in this case, numerous more energetic gamma rays of ^{214}Bi. The counting efficiency of this gamma ray must be determined for the specific Ge detector dimensions and sample location.

Safety Reminder

- Follow the usual safety procedures when working in a radiological laboratory.
- Caution should be exercised when preparing and working with corrosive mineral acids.
- All liquids and solids are to be properly disposed according to laboratory rules and protocol.

Equipment

- 10-mL and 1,000 mL graduated cylinders
- Borosilicate beaker, 1- 2-, or 4-L
- Beakers, 100 mL
- Stirring rods, glass
- Pipette, 5 mL

- Pipetter capable of measuring tenths of mL
- Heated magnetic stirrer and stir bar
- Analytical balance (capable of weighing to nearest 0.01 mg)
- Filtering apparatus
- Filter circles (Whatman 42, 2.5 cm diameter or suitable size for filtering apparatus)
- Ring and Disk mount
- Mylar film cover
- Vacuum pump
- Reagent bottles
- Sintered-glass crucible, fine porosity
- Drying oven
- Plastic squirt bottle for deionized water

Note: All glassware for the experiment should be acid-washed and rinsed with deionized water before use.

Reagents

- ^{226}Ra standard solution, diluted to concentration of about 40 Bq per mL, in 0.01 N HNO_3
- ^{228}Ra standard solution, diluted to concentration of about 40 Bq per mL, in 0.01 N HNO_3
- Concentrated HNO_3
- Concentrated HCl
- Concentrated H_2SO_4
- Barium chloride: Reagent grade $BaCl_2.2H_2O$
- Barium carrier, standardized, 9 mg Ba^{2+}/mL: Dissolve 16.01 g of $BaCl_2.2H_2O$ in deionized water, add 5 mL of concentrated nitric acid, and dilute to 1 L with deionized water. (See **Barium Carrier Standardization** at end of Part 8C.)
- Sulfuric acid, 18 N: Cautiously add 500 mL of concentrated sulfuric acid to 400 mL of deionized water and dilute to 1 L with deionized water. *Note: The reaction of concentrated sulfuric acid with water is an extremely exothermic one. Add concentrated sulfuric acid to water in small quantities, with stirring.*
- Sulfuric acid, 0.01 N: Add 0.55 mL of 18 N H_2SO_4 to 100 mL deionized water and dilute to 1 L.
- Ethanol, 95%
- Diethyl ether

8A. Determination of Radium in Drinking Water

Procedure

Step 1. Measure the volume of preserved drinking water in a large graduated cylinder and record the volume to the nearest 1 mL. The sample should have been preserved with 4 mL of concentrated HNO3 per gallon (3.7 L) of drinking water or enough concentrated HNO_3 to make the pH of the water < 2.

Transfer to a beaker. *The instructor will specify the quantity of water in the sample.*

Step 2. Add 10 mL of concentrated HCl for every liter of water used and mix thoroughly.

Step 3. Accurately pipette 5.0 mL of barium carrier (9 mg/mL) into the sample. Stir and heat to boiling.

Step 4. Precipitate barium sulfate by adding 10 mL of 18 N H_2SO_4 in a fine stream while stirring. Record the date and time of precipitation. Cool 30 minutes in an ice bath or allow overnight settling in covered beaker.

Date and time of $BaSO_4$ precipitation: _____

Note: The following steps describe a specific method of filtering, weighing and mounting the sample. The instructor may provide alternate instructions for preparing the barium sulfate source appropriate for the available counting facilities.

Step 5. Filter the solution that contains the $BaSO_4$ through a tared filter. One approach is to let the precipitate settle and then decant carefully approximately 800 mL of a 1-L sample; slurry the precipitate in the remaining water, pour it through the filter; and wash any remaining precipitate from the beaker to the filter with a jet of deionized water. *Avoid pulling excess air through the filter because airborne radon progeny will add to the sample counting results (see Part 8B).*

Step 6. Wash and dry the precipitate on the filter with 10 mL of ethanol, followed by 10 mL of diethyl ether. Turn off the suction as the last of the diethyl ether passes through the filter.

Step 7. Remove the dried filter with the precipitate. Weigh the tared filter on a tared planchet to the nearest 0.1 mg. Record the weight in Data Table 8.1

Step 8. Mount the precipitate in a holder such as a ring and disk with Mylar cover. Label the sample according to counting room protocol.

Step 9. Count immediately for 60,000 s with a Ge detector plus gamma-ray spectrometer to observe the gamma rays emitted by the ^{228}Ra daughter in the sample if these results are needed promptly. Count after 2 – 4 weeks to permit ingrowth of the ^{226}Ra progeny and determine the levels of both ^{226}Ra and ^{228}Ra. Record mid-time of counting. Record net count rates in energy regions of interest in Data Table 8.2 and 8.3.

Dates and mid-times of counting: _____

Chemical Yield Calculation

Subtract the tared filter paper plus planchet weight from the combined weight of the filter, planchet, and precipitate to determine the net weight of the $BaSO_4$ precipitate. Enter result in Data Table 8.1 Divide this net weight of the precipitate by the theoretical weight of the precipitate based on the amount of

standardized barium carrier that is used in the precipitate. This is the chemical yield (Y_s) for the sample precipitate.

Data Table 8.1 Chemical yield

	Mass
Filter Paper + Precipitate + planchet	
Filter Paper + planchet	
Barium Carrier (as $BaSO_4$)	

$$\frac{\textit{Final mass of barium sulfate}}{\textit{Initial mass of barium sulfate}} = \textit{chemical yield} \qquad (8.1)$$

Chemical Yield = _____

Counting

After the selected ingrowth period, record the time and count the sample according to the counting procedures. The count time may be adjusted if the radium concentration is higher than usual or the detector counting efficiency is unusually high or low.

Ingrowth interval: _____

Treatment of Gamma-Ray Counting Data

Radium-226 Concentration Calculation

Determine the amount of ^{226}Ra according to the following equation for the 351.9 keV gamma-ray of the progeny ^{214}Pb and the 609.3 keV gamma-ray of the progeny ^{214}Bi, respectively.

$$A_s = \left[\frac{1}{(0.037)VY_sD_s\varepsilon}\right]\left(\frac{R}{F_i}\right) \qquad (8.2)$$

Where

A_s = the concentration of ^{226}Ra in pCi/L,

0.037 = conversion factor from disintegrations per second to picocuries (pCi) [0.037 dps = 1 pCi],

Y_s = chemical yield determined for the sample,

D_s = ingrowth factor $(1 - e^{-\lambda t})$, where $\lambda = 0.693/t_{1/2}$; t = time interval in d between the separation of the radium from the water and the midpoint of the counting time, and $t_{1/2}$ = half life of ^{222}Rn of 3.82 d,

R = net counts per s for the gamma-ray under consideration (background and Compton contributions have been subtracted; the uncertainty or error reported for that gamma ray should be noted),

F_i = branching ratio for gamma-ray under consideration; see Data Table 8.2 for value,

ε = counting efficiency of specific gamma ray; see Part 8.C for measurement, and
V = sample volume, L.

Record all information in DataTable 8.2 Based on the values calculated for each gamma-ray and their respective uncertainties, calculate a weighted average for the two. See section on **Weighted Average Calculations** in Appendix 6. Report the value as pCi or Bq ^{226}Ra per L water with its uncertainty.

Data Table 8.2 Activity of ^{226}Ra

^{226}Ra	351.9 keVγ	609.3 keVγ
Sample volume (V)		
Chemical Yield Fraction (Y)		
Ingrowth factor (D)		
Net gamma ray count rate (R)		
Branching ratio (F_i)	0.358	0.448
Counting efficiency (ε)		
Activity ^{226}Ra (pCi/L ± σ)		

Activity ^{226}Ra in pCi/L (weighted average)_____

Radium-228 Concentration Calculation

Determine the amount of ^{228}Ra according to the above equation, but for the 338.3 keV and 911.2 keV gamma-rays of the progeny ^{228}Ac. The following items are different from the above equation for ^{226}Ra:

D_s refers to the ^{228}Ac half-life of 6.15 h, but parent and daughter are in equilibrium (D_s = 1.00) immediately because both are co-precipitated with barium sulfate.

F_i refers to the branching ratios of the two characteristic gamma rays of ^{228}Ac that are shown in Data Table 8.3

Record the data for this set of calculations in Data Table 8.3 Based on the values calculated for each gamma-ray and their respective uncertainties, calculate a weighted average for the two. See section on **Weighted Average Calculations** in Appendix 6. Report the value as pCi or Bq ^{228}Ra per L water with its uncertainty.

Data Table 8.3 Activity of ^{228}Ra

^{228}Ra	338.3 keVγ	911.2 keVγ
Sample volume (V)		
Chemical Yield Fraction (Y)		
Ingrowth factor (D)		
Net gamma ray count rate (R)		
Branching ratio (F_i)	0.113	0.266
Counting efficiency (ε)		
Activity ^{228}Ra (pCi/L ± σ)		

Activity ^{228}Ra in pCi/L (weighted average)_____

8B. Preparation of a Reagent Blank and Testing for Airborne Radon and Progeny

Procedure

Note: If both the reagent blank and testing for airborne radon progeny are to be done, perform the two samples in parallel. Make certain that glassware could not have accumulated radon progeny from air while standing in the open.

Step 1. *Reagent blank.* Measure a 1-liter volume of deionized water. Add 1 mL of concentrated HNO_3 to the sample. Pour the measured volume into a clean borosilicate beaker large enough to contain it without spilling, e.g., 2-L volume.

Step 2. Add 10 mL of concentrated HCl to the deionized water and mix thoroughly.

Step 3. Accurately pipette 5.0 mL of barium carrier (9 mg/mL)into the sample. Stir and heat to boiling.

Step 5. Precipitate barium sulfate by adding slowly 10 mL of 18 N H_2SO_4 in a fine stream with stirring. Record date and time of separation of radon daughter plus progeny from radium parent. Cool 30 minutes in an ice bath or allow to digest overnight covered..

Note: The following steps describe a specific method of filtering, weighing and mounting the sample. The instructor may provide alternate instructions for preparing the barium sulfate source appropriate for the available counting facilities.

Date and time of radium separation:_____

Step 6. Place a tared filter of the type and dimensions used in Procedure 8A in the filter funnel apparatus that is attached to a vacuum source.

Step 7a. *For reagent blank.* Filter the $BaSO_4$ solution on the tared filter paper. Keep filtration time to a minimum and measure the total time that the air is drawn through the filter. Wash the precipitate that remains in the beaker to the filter by rinsing the beaker with a jet of deionized water. Wash and dry the precipitate on the filter with 10 mL of ethanol, followed by 10 mL of diethyl ether. Turn off the suction when the final amount of diethyl ether has passed through the filter.

OR

Step 7b. For *detection of airborne radon progeny.* Filter a reagent blank solution that contains the $BaSO_4$ on the tared filter paper. Wash the precipitate that remains in the beaker to the filter by rinsing the beaker with a jet of deionized water. Wash and dry the precipitate on the filter with 10 mL of ethanol, followed by 10 mL of diethyl ether. Draw air through the sample for a measured time of 30 minutes to 1 hour to collect airborne radon and

Data Table 8.4 Chemical yield of blank and airborne sample

	Blank	Airborne Sample
Filter Paper + Precipitate, mg		
Filter Paper, mg		
Barium Carrier (as precip. $BaSO_4$), mg		
Chemical Yield		

daughters. Record date, time of collection of radon progeny from air, and collection period.

Date, time, and period of collection of radon progeny from air: _____

Step 8. Remove the filter with the precipitate. Weigh the tared filter on a tared planchet the nearest 0.1 mg. Record the weight in Table 8.4

Step 9. Mount the precipitate on a holder such as a ring and disk, and cover with Mylar film. Label the sample according to counting room protocol.

Step 10. Count the gamma rays emitted by the sample with a Ge detector plus spectrometer after the same time interval as in Procedure 8A. The airborne radioactivity sample should be counted as soon as possible after sample collection, with data recorded in Data Table 8.5 Repeat counting after selected intervals and record in Data Table 8.6, as indicated below. Determine the chemical yield as described in Procedure 8A, based on the information recorded in Data Table 8.4

Counting

Reagent Blank. Inspect the gamma-ray spectrum carefully to determine if any of the gamma-rays from radium-226 are present. If so, record results in Data Table 8.5 Determine the amount according to the process described in Part 8A.

Activity ^{226}Ra in pCi/L (weighted averages): _____

Airborne Radon Progeny. Scheme 1. Count the sample immediately on the germanium detector, recording the time interval from separation to filtration Record in Data Table 8.5 Then count again in one week, followed by a third

Data Table 8.5 Activity of ^{226}Ra in blank and airborne sample

	351.9 keV	609.3 keV	351.9 keV	609.3 keV
Sample volume (V)	Blank		Airborne Sample	
Chemical Yield Fraction (Y)				
Ingrowth factor (D)				
Net gamma ray count rate (R)				
Branching ratio (F_i)	0.358	0.448	0.358	0.448
Counting efficiency (ε)				
Activity ^{226}Ra (pCi/L $\pm$ σ)				

Data Table 8.6 Gamma-ray decay study of radionuclides on filters

Gamma-ray energy and net count rate interval, d	Count 1		Count 2		Count 3	
	351.9	609.3	351.9	609.3	351.9	609.3

Data Table 8.7 Alpha- and beta-particle decay study

Interval, d	Gross α (cps)	Bkgd. α (cps)	Net α (cps)	Gross β(cps)	Bkgd. β(cps)	Net β(cps)

count in two weeks after sample collection. Be sure to compare the spectrum of the sample to a detector background spectrum counted the same length of time. Record results in Data Table 8.6. Identify the radionuclides by gamma ray spectrometry.

Scheme 2. Count the sample immediately with an α and β counter (e.g., the proportional counter) for 200 minutes. Repeat the count each day for 14 days or until the count rate equals or nearly equals the background. Obtain background counts for both alpha-particle and beta-particle counting modes. Subtract respective backgrounds for each count period and record in Data Table 8.7

Plot data of alpha-particle and beta-particle net count rates (on log scale) on the same graph versus time (linear scale) in days.

8C. Preparation of ^{226}Ra *and* ^{228}Ra *Standard and Barium Carrier*

Procedure

Preparation and counting of ^{226}Ra and ^{228}Ra standards for calibration of Ring and Disk source *(in triplicate)*

Step 1. Pipette exactly 5 mL of barium carrier into 100-mL beaker that contains 20 ml of deionized water. Add 5 drops of concentrated HCl. Pipette 1 ml of ^{226}Ra standard solution and also pipette 1 mL of ^{228}Ra standard solution into the beaker. Stir well.

Data Table 8.8 Radium count rate

	^{226}Ra		^{228}Ra	
Energy (keV)	351.9 γ	609.3 γ	338.3 γ	911.2 γ
Decay fraction	0.358	0.448	0.113	0.266
Yield (fraction)				
Activity (dps)				
Gross count rate (cps)				
Net count rate (cps)				
Count rate, ingrowth corrected (cps)				
Counting efficiency				

Step 2. Heat the solution to boiling and add 20 ml of 18 N H_2SO_4 in a steady stream with stirring to precipitate $BaSO_4$ with radium standards. Digest while boiling for 10 minutes. Let solution cool.

Date and time of precipitation: _____

Step 3. Pour slurry through tared filter circle in filtering apparatus. Rinse beaker with four 5-mL portions of 0.01 N H_2SO_4 onto filter. Wash and dry filter and precipitate with 10 mL of ethanol and then with 10 ml of diethyl ether.

Step 4. Transfer filter to tared planchet and weigh. Subtract tared weights to calculate weight of $BaSO_4$ and the yield of $BaSO_4$ relative to the pipetted amount. Record yield in Data Table 8.8 Prepare filter on a holder such as a ring and disk with Mylar film cover. Store for counting.

Step 5. After interval of about 4 weeks since $BaSO_4$ precipitation, count filter in holder with Ge detector and spectrometer for at least 3,000 s. Make certain that location of holder relative to the detector is identical for this calibration measurement and all sample measurements.

Step 6. Record the gross count rates of all four characteristic peaks in Data Table 8.8 Calculate the net count rate for each peak. Use equation 8.2 (given in Procedure 8A) to calculate the counting efficiency, ε, for each of the four gamma rays; this is based on the activity, A_s, of each of the two standard solutions in the pipetted solution volume, V (i.e., 1 mL). The ingrowth factor, D_s, is 1.00 for ^{228}Ra and 0.99 for ^{226}Ra when the interval between radium precipitation and counting is 26 days. Calculate the average counting efficiency and standard deviation.

Barium carrier standardization *(in triplicate)*

Step 1. Pipette exactly 5.0 mL of carrier into a clean 100-mL beaker that contains 20 mL of deionized water. Add 5 drops of concentrated HCl. Heat the solution to boiling and add 20 mL of 18 N H_2SO_4 in a steady stream with stirring. Digest the sample on the hot plate for 10 minutes. Remove the beaker from the hot plate and let the solution cool to room temperature.

Step 2. Slurry the precipitate and filter into a clean, tared sintered-glass crucible of fine porosity. Rinse beaker with four 5-mL portions of 0.01 N H_2SO_4 and add to filter to ensure quantitative transfer of all of the precipitate to the crucible. Wash the precipitate twice with 20 mL of 0.01 N H_2SO_4.
Step 3. Remove the crucible from the filtering funnel and dry in the oven at 110°C for 2 hours.

Step 4. Place the crucible in a desiccator to cool. Weigh to constant weight. Record the weight for calculating the barium mass per mL. Report the average standardized barium in mg Ba^{2+}/mL and as $BaSO_4$/mL (to the nearest 0.1 mg) and label bottle (see Experiment 5). The spread in the values should be less than 1%.

Net weight of $BaSO_4$: (1)_____; (2)_____ ;(3)_____; (average)_____

Questions

1. If a sample contains 0.56 pCi ^{226}Ra per L, (a) calculate the mg/L of ^{226}Ra in the water. (b) Calculate the mg/L of natural uranium that would be in the water if the ^{226}Ra is in radioactive equilibrium with its parent ^{238}U.
2. List the assumption(s) associated with the reported chemical yield for the recovery of radium by its co-precipitation on $BaSO_4$. Design an experiment to test assumptions.
3. If the chemical yield for several samples is in excess of 100%, offer plausible explanations that would give rise to this observation. How would you correct or compensate for this observation?
4. Three different laboratories conduct an experiment to determine the amount of airborne radioactivity on $BaSO_4$. Laboratory A finds no activity; B observes both alpha and beta activity that decay with a half life of several days; C observes alpha and beta activity that increase with time. Explain their disparate findings.
5. If airborne activity is a serious and troublesome problem for a laboratory, suggest ways to eliminate or minimize it.
6. Calculate the amount of barium carrier that will remain in a 4-L sample, as described here. What percent barium is lost due to its solubility? Design an experiment to check this result. See the introduction for the solubility product value.

Source

Adapted from "Method for the Determination of Radium-228 and Radium-226 in Drinking Water by Gamma-ray Spectrometry Using HPGE or Ge(Li) Detectors", ERC, GTRI, Georgia Institute for Technology, Atlanta, GA, an Approved Test Procedure of the US EPA (see Federal Register, March 12, 2007, pp. 11,200–11,249).

STATE OF ILLINOIS)
) SS
COUNTY OF SANGAMON)

PROOF OF SERVICE

I, the undersigned, on oath state that I have served the attached Illinois Environmental Protection Agency's Comments upon the person to whom it is directed, by placing it in an envelope addressed to:

TO: John Therriault, Clerk
Illinois Pollution Control Board
James R. Thompson Center
100 W. Randolph, Suite 11-500
Chicago, IL 60601

General Counsel
Illinois Dept. Of Natural Resources
One Natural Resources Way
Springfield, IL 62702-1271

Matt Dunn, Environmental Bureau Chief
Office of the Attorney General
69 West Washington Street, Suite 1800
Chicago, IL 60602

and mailing it First Class Mail from Springfield, Illinois on November 7, 2008, with sufficient postage affixed.

SUBSCRIBED AND SWORN TO BEFORE ME
this 7th day of November, 2008

Notary Public

OFFICIAL SEAL
DAWN A. HOLLIS
NOTARY PUBLIC, STATE OF ILLINOIS
MY COMMISSION EXPIRES 8-19-2012

THIS FILING IS SUBMITTED ON RECYCELD PAPER