



Designation: D5174 – 23

Standard Test Method for Trace Uranium in Water by Pulsed-Laser Phosphorimetry¹

This standard is issued under the fixed designation D5174; 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.

1. Scope

1.1 This test method covers the determination of total uranium, by mass concentration, in water within the calibrated range of the instrument, 0.1 $\mu\text{g/L}$ or greater. Samples with uranium mass concentrations above the laser phosphorimeter dynamic range are diluted to bring the concentration to a measurable level.

1.2 This test method was used successfully with reagent water. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

1.3 The values stated in SI units are to be regarded as the standard.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 ASTM Standards:²

[D1129 Terminology Relating to Water](#)

[D1193 Specification for Reagent Water](#)

[D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water](#)

[D3370 Practices for Sampling Water from Flowing Process Streams](#)

[D4448 Guide for Sampling Ground-Water Monitoring Wells](#)

[D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis](#)

[D6001 Guide for Direct-Push Groundwater Sampling for Environmental Site Characterization](#)

[E131 Terminology Relating to Molecular Spectroscopy](#)

3. Terminology

3.1 Definitions:

3.1.1 For definitions of terms used in this test method, refer to Terminologies [D1129](#) and [E131](#).

3.1.2 For terms not defined in this test method or in Terminology [D1129](#) or [E131](#), reference may be made to other published glossaries.³

4. Summary of Test Method

4.1 This test method is based on the utilization of a laser phosphorimeter to determine total uranium, by mass, in water samples.

4.2 A sample aliquant is pipetted into a pretreated glass vial. Concentrated HNO_3 and hydrogen peroxide are added and the sample heated to dryness. This step is repeated as necessary and the residue is dissolved in dilute HNO_3 . A complexant is added to an aliquant of this sample and analyzed in the phosphorimeter.

4.3 For screening purposes only, an aliquant of the sample may be pipetted directly into the phosphorimeter cell containing uranium complexant and read. This cannot be done if the sample was preserved with HCl or if the matrix is not known.

5. Significance and Use

5.1 This test method is useful for the analysis of total uranium in water following wet-ashing, as required, due to impurities or suspended materials in the water.

6. Interferences

6.1 *Absorption (Inner Filter Effect)*—This effect is more severe with ultraviolet excitation light (337 nm) than with visible excitation because many prevalent compounds have pi-bonding and absorb strongly in this region. Ferric iron and

¹ This test method is under the jurisdiction of ASTM Committee [D19](#) on Water and is the direct responsibility of Subcommittee [D19.04](#) on Methods of Radiochemical Analysis.

Current edition approved June 1, 2023. Published July 2023. Originally approved in 1991. Last previous edition approved in 2013 as D5174 – 07 (2013) which was withdrawn January 2022 and reinstated in June 2023. DOI: 10.1520/D5174-23.

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.

³ See *American National Standard Glossary of Terms in Nuclear Science and Technology* (ANSI N1.1), available from American National Standards Institute, 1430 Broadway, New York, NY 10014, www.ansi.org.

oxy-anions such as nitrate and organic acids are examples. Visible excitation (425 nm) may be absorbed by yellow solutions, for example, chromate. The consequences of this may be reduced signals and low analysis results.

6.2 *Lumiphors*—Many organic substances, such as humic acids and organic degradation products from incomplete ashing emit luminescence of varying lifetimes after excitation. An advantage of kinetic phosphorescence measurement is the ability to determine if interferences are present by observing the lifetime of the decay.

6.3 *Quenching*—Shortened triplet-state lifetime and reduced phosphorescence intensities of the excited uranyl complex result when quenching occurs. Reliable results cannot be obtained when quenching exceeds 80 % to 90 %. Reducing agents such as alcohols, halides except fluoride, and metals with electronic energy levels overlapping those of uranyl ion are strong quenching agents; examples are silver, lead, iron (II), manganese (II), and thallium. Results from single time-gated instruments are particularly sensitive to even mild quenching agents such as aluminum (III), magnesium (II), calcium (II), and strontium (II).

6.4 *Competing Reactions*—For this test method to perform well, the uranyl ion must be protected from various intermolecular mechanisms which rapidly quench the uranyl luminescence. Complexation fulfills this need and examples of effective agents are phosphoric acid, polyphosphates, and Uraplex.⁴

6.5 Hydrochloric acid, if present, is an interference unless eliminated during digestion.

6.6 If the concentration of uranium in the samples exceeds the calibrated range of the instrument, samples are diluted 1/100 (or otherwise as appropriate) in 0.8 M nitric acid.

6.7 When concentrations of interferences in the samples prevent obtaining an acceptable measurement, samples are diluted in 0.8 M nitric acid to minimize the effects of the interferences.

7. Apparatus

7.1 *Laser Phosphorimeter*,⁴ meeting the following criteria:

7.1.1 *Detection Limit*—The MDL for uranium is generally 0.1 µg/L or less.

7.1.2 *Dynamic Range*—The phosphorimeter must handle an analytical range of 400 or greater.

7.1.3 *Instrumental Precision*—The precision of repetitive measurements sufficient to obtain a relative standard deviation of less than 15 % at the low points of the calibration curves.

7.2 *Labware*—If samples containing less than 0.1 µg/L uranium are to be analyzed, digestion vessels (both TFE-fluorocarbon and glassware) if used, and liquid scintillation vials should be leached in 4 M nitric acid and rinsed thoroughly

with deionized water before using. This is necessary to reduce sample contamination from leachable uranium.

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.⁵ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagent blanks shall be run with all determinations.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193, Type I or better.

8.3 *Hydrogen Peroxide*—Standard 30 % solution of hydrogen peroxide (H₂O₂); commercially available reagent grade.

8.4 *Nitric Acid*—(sp gr 1.42) concentrated nitric acid (HNO₃).

8.5 *Nitric Acid 4 M*—Add 250 mL of concentrated nitric acid (HNO₃) to 500 mL of reagent water and dilute to 1 L in reagent water, Type I or better.

8.6 *Nitric Acid 0.8 M*—Add 50 mL of concentrated nitric acid (HNO₃) to 500 mL of reagent water and dilute to 1 L in reagent water, Type I or better.

NOTE 1—Reagent blank shall be run on the nitric acid to analyze for the level of uranium.

8.7 *Uranium Complexant*—Phosphoric acid or Uraplex⁴ are some complexants that may be used.

9. Calibration and Standardization

9.1 *Preparation of Standards and Sample for Laser Measurement*—Standards and samples shall be prepared in a similar matrix for phosphorimetric measurement. The final sample preparation step puts uranium into a 0.8 M HNO₃ matrix. Use uranium standards traceable to the SI through a national metrology institute such as NIST or NPL.

9.2 *Calibration of Phosphorimeter*—The instructions for the operation of the laser phosphorimeter are provided by the manufacturer. The phosphorimeter should be calibrated each day of use and the calibration verified with standards obtained from a different stock solution than used to prepare the calibration standards.

10. Sampling

10.1 Collect the sample in accordance with the applicable methods as described in Practices D3370, D4448, and Guide D6001 or other approved practices or guides.

⁴ The sole source of supply of the apparatus known to the committee at this time is Chemchek Instruments, Inc., 1845 Terminal Drive, Suite #101, Richland, WA, 99354-4959. Consult appropriate equipment manuals for explanations of calibration and calculations. 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.

⁵ *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, American Chemical Society, 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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

11. Procedure

11.1 Pipet 5.0 mL of sample into a glass vial previously treated as described in 7.2.

11.2 Add 1 mL of concentrated HNO₃ and two or three drops of 30 % hydrogen peroxide.

11.3 Place the vial on a hot plate and heat to dryness. Take care that spattering of the sample does not occur.

NOTE 2—Placing the vial in a 50 mL beaker makes it easier to handle and not so apt to be knocked over.

11.4 Remove the vials from the hot plate and add 1 mL of concentrated HNO₃, two or three drops of 30 % hydrogen peroxide, and heat to dryness. Repeat as necessary until only a white or translucent residue remains.

11.5 Add 1.0 mL of 4 M HNO₃ and warm gently, if necessary, to dissolve the residue. Then add 4.0 mL of water conforming to Specification D1193, Type I or better. Swirl to mix thoroughly.

11.6 Analyze the solution according to the instruction manual provided with the phosphorimeter.

NOTE 3—If the concentration of uranium in the prepared sample falls above the calibrated range of the instrument, dilutions should be made using 0.8 M HNO₃, used for the final sample preparation.

NOTE 4—Lifetime values below 200 μs indicate significant quenching in the sample and could affect the quality of results obtained. The problem can often be addressed by diluting samples in 0.8 M HNO₃.

12. Calculation

12.1 Refer to the instrument manual for explanation of calculations.

12.2 Estimate the uncertainty of analysis by preparing and analyzing replicate analyses at different known concentrations and calculating the bias and standard deviation as a function of concentration.

12.3 Estimate the method detection limit (MDL) and method reporting limit (RL) on a periodic basis or following major maintenance of the instrument by processing seven or more replicate reagent blanks through the entire above method above. Calculate the standard deviation S_B and the MDL as described in Eq 1 and Eq 2 below.

NOTE 5—Software supplied with certain KPA instruments excludes data in time gates where net signal intensity falls to zero or below. Further, the software censors final concentration results (that is, reports as “less than” values) when there is insufficient net intensity data to perform a best-fit regression to the decay plot. As a result, during the analysis of blanks the instrument will often yield non-numerical concentration results (that is, “less-than” values). In such cases, “positive” results may be induced by spiking the MDL study “blank” samples at a concentration approximately 2 to 5 times the estimated/calculated MDL. MDL target concentrations should be adjusted and study measurements be repeated iteratively until a satisfactory concentration for an MDL is obtained.

$$MDL_{0.99} = t_{\text{Stud}} \cdot S_B \quad (1)$$

$$S_B = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n - 1}} \quad (2)$$

where:

$MDL_{0.99}$ = the method detection limit at the 99 % confidence level,

S_B = standard deviation of the measured mass concentrations of uranium in replicate blanks (μg/L),

t_{Stud} = 99th percentile of Student’s t -distribution with $n - 1$ degrees of freedom (default = 3.143 for 6 degrees of freedom),

n = number of blanks analyzed in the study (default = 7),

x_i = measured mass concentrations of uranium in the i^{th} blank, and

\bar{x} = mean of the measured mass concentrations of uranium in all replicate blanks (μg/L).

12.4 Method Reporting Limit (RL):

12.4.1 The method reporting limit (RL) is defined as the lowest non-zero standard on the calibration curve or the calculated MDL.

12.4.2 The RL shall never be established at a mass concentration below the MDL and typically is established at concentrations 3 to 10 times the concentration of the measured MDL.

12.5 Reporting Results:

12.5.1 All sample results and reporting limits shall be adjusted for any dilutions performed.

12.5.2 The sample result and associated reporting limit for each result equal to or greater than the RL shall be reported.

12.5.3 Sample results measured below the low point on the calibration curve shall be reported as “less than the reporting limit” (for example, < RL).

13. Precision and Bias⁶

13.1 The collaborative test conducted on this test method included six laboratories for Level 1 and seven laboratories for Levels 2 and 3. There were a total of three levels between 1 μg/L and 100 μg/L with three replicates per level. The determination of the precision and bias statements were made in accordance with Practice D2777.

13.2 These collaborative test data were obtained using reagent grade water. For other matrices, these data may not apply.

13.3 The bias of this test method, based upon the collaborative test data, was found to vary with level according to Table 1.

13.4 The overall and single operator precision were found to vary with level according to Table 2.

14. Quality Control

14.1 In order to be certain that analytical values obtained using this test method are valid and accurate within the confidence limits of the test the following QC measures shall be followed when running the test. The batch size should not exceed 20 samples, not including QC samples.

⁶ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1148. Contact ASTM Customer Service at service@astm.org.