Designation: D5174 – 07 (Reapproved 2013)

Standard Test Method for
Trace Uranium in Water by Pulsed-Laser Phosphorimetry[1]

1. Scope

1.1 This test method covers the determination of total uranium, by concentration, in water within the calibrated range of the instrument, 0.1 µg/L or greater. Samples with uranium by mass, levels 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 and health practices and determine the applicability of regulatory limitations prior to use.*

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 Closed Conduits
D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water
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 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

---

[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 Jan. 1, 2013. Published January 2013. Originally approved in 1991. Last previous edition approved in 2007 as D5174 – 07. DOI: 10.1520/D5174-07R13.

[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.

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 (H_2O_2); commercially available reagent grade.

8.4 *Nitric Acid*—(sp gr 1.42) concentrated nitric acid (HNO_3).

8.5 *Nitric Acid 4 M*—Add 250 mL of concentrated nitric acid (HNO_3) to 500 mL of reagent water and dilute to 1L in reagent water, Type 1 or better.

8.6 *Nitric Acid 0.8 M*—Add 50 mL of concentrated nitric acid (HNO_3) to 500 mL of reagent water and dilute to 1L in reagent water, Type 1 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 Uraplex[4] 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 HNO_3 matrix. Use uranium standards traceable to a National Standardizing Laboratory 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.

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 HNO_3 and two or three drops of 30 % hydrogen peroxide.

---

[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] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual 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.

11.3 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 HNO_3, 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 HNO_3 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 HNO_3, used for the final sample preparation.

NOTE 4—Lifetime values below 200 us 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 HNO_3.

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 2–5 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.

$$MDL_{0.99} = t_{Stud} \cdot S_B \tag{1}$$

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

where:

$MDL_{0.99}$ = the method detection limit at the 99 % confidence level,
S_B = standard deviation of the mean of measured concentration of uranium in replicate blanks in concentration (µg/L),
t_{Stud} = student’s t value at the 99 % confidence level for 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 concentration of uranium in blank “i,”
$\bar{x}$ = mean of measured concentration of uranium in all replicate blanks in concentration (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 concentration below the MDL and typically is established at concentrations 3–10 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 Bias[6]

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 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.

TABLE 1 Uranium in Water by Phosphorimetry (Digestion Method) Bias Data

Amount Added, µg/L	Amount Found, µg/L	Bias, %
2.25	2.26	0.44
42.30	43.18	2.08
84.60	89.11	5.33

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.

TABLE 2 Uranium in Water by Phosphorimetry (Digestion Method) Pooled Single Operator Precision (S_o) and Overall Precision (S_t)

Amount Added, µg/L	S_o, µg/L	S_t, µg/L
2.25	0.09	0.27
42.30	1.41	2.48
84.60	1.98	5.53

14.2 *Calibration and Calibration Verification:*

14.2.1 The calibration is performed each day of use.

14.2.2 A minimum of three standards of different concentrations are analyzed to prepare a calibration curve for the low and high measurement ranges respectively. The concentrations for the low and high ranges depend on the instrument used with typical values being 0.1–10 µg/L and 10–300 µg/L respectively. The low standard of each curve shall always be equal to or greater than the method detection limit.

14.2.3 A calibration verification standard prepared at near the midpoint concentration within each calibration range is analyzed prior to the initiation and at the conclusion of each analysis batch.

14.2.4 The acceptance range for the recovery of the calibration verification standard recovery is 90–110 % of the expected value. If the result for the calibration verification standard falls outside the acceptance range, recalibrate the instrument and reanalyze samples back to the last valid calibration verification standard.

14.3 *Initial Demonstration of Instrument Capability:*

14.3.1 If a laboratory has not performed this test before, or if there has been a major change in the measurement system such as a significant software change or a new instrument, etc., a precision and bias study shall be performed to demonstrate instrument capability.

14.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material (IRM) containing accurately known concentrations of approximately 2, 40 or 80 µg/L of uranium.

14.3.3 Calculate the mean and standard deviation of the values obtained from the analysis and compare to the laboratory specified acceptable ranges of precision and bias, to those in the following table or to those specified by the customer. This study should be repeated until the precision and the mean recovery is within the specified limits. If a concentration other than the recommended concentration is used, refer to Test Method D5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

Amount Added, µg/L	Precision (S_o), %	Bias (S_t), %
2.25[A]	4.0	12.0
42.3[A]	3.3	5.9
84.6[A]	2.3	6.5

[A] The collaborative test conducted on this test method included six laboratories for Level 1 and seven laboratories for Levels 2 and 3.

14.3.4 If this demonstration is performed to confirm instrument performance, verify that the method detection limit has not changed.

14.4 *Demonstration of Capability :*

14.4.1 To demonstrate capability each analyst must analyze a blank and four replicates of a standard solution prepared from an IRM containing accurately known concentrations of approximately 2, 40 or 80 µg/L of uranium or concentrations acceptable to the customer. The matrix and chemistry should be equivalent to the samples to be analyzed. Each replicate and the blank must be taken through the complete analytical test method including any sample preservation and pretreatment steps.

14.4.2 Compare the results of the replicates and the blank to the laboratory or customer control limits. If the results are not within the control limits repeat the analyses.

14.5 *Laboratory Control Sample (LCS):*

14.5.1 To ensure that the test method is in control, analyze a LCS with each batch of no more than 20 samples. The concentration added to reagent water should be appropriate for the type of samples analyzed and allow sufficient precision to ensure a meaningful assessment of accuracy. The LCS must be taken through all the steps of the analytical method including sample preservation and pretreatment. The result obtained for the LCS shall fall within the limit of ±25 % of the expected value or within a limit that is compliant with the data quality objectives or the applicable regulations.

14.5.2 If the result is not within these limits, reporting of the results is halted until the problem is resolved. An indication of the occurrence should accompany the reported results.

14.6 *Method Blank:*

14.6.1 Analyze a reagent water test blank with each batch of no more than 20 samples. The concentration of analyte found in the blank should be less than the reporting limit. If the concentration of the analyte is found above this level, the results must be flagged.

14.7 *Matrix Spike:*

14.7.1 Prepare at least one matrix spike sample with each batch of no more than 20 samples by spiking a second, like-sized aliquant of one of the samples within the batch with a known concentration of uranium. Prepare and analyze the matrix spike sample in the same manner as the other samples in the batch.

14.7.2 The spike should produce a concentration of uranium that is at least 2 to 5 times the anticipated sample concentration or as specified by the laboratory, whichever is greater.

14.7.3 Calculate the percent recovery ($\%Rec_{MS}$) of the matrix spike using the following formula:

$$\%Rec_{MS} = \frac{A_{AS} - A_A}{A_S} \times 100 \quad (3)$$

where:

$\%Rec_{MS}$ = percent recovery of the matrix spike,
A_{AS} = analyte plus spike concentration (µg U / L sample),
A_A = analyte concentration (µg U / L sample), and
A_S = spike amount (µg U / L sample).

14.7.4 The matrix spike recovery should fall within the range of 50 % to 150 % of the expected value. If the concentration is not within these limits, provide an explanation in the case narrative.

14.8 *Duplicate:*

14.8.1 Prepare and analyze at least one sample in duplicate with each batch of no more than 20 samples.

14.8.2 In the absence of laboratory specified control limits, compare to the single operator precision using an F test.

14.8.3 If the result exceeds the precision limit, the results must be flagged.

14.9 *Independent Reference Material (IRM):*

14.9.1 Analyze an IRM, such as a performance evaluation sample, at least once per quarter. The result must fall within the laboratory specified control limits. If the result falls outside the laboratory specified limits corrective actions need to be considered.

15. Keywords

15.1 kinetic phosphorimetry; laser; phosphorescence; uranium ; water

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the ASTM website (www.astm.org/COPYRIGHT/).