



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

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1. Scope

1.1 This test method covers the determination of total uranium, by mass, in water in the range of 0.05 ppb or greater. Samples with uranium by mass, levels above the laser phosphorimeter dynamic range may be 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:

D 1129 Terminology Relating to Water²

D 1193 Specification for Reagent Water²

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water²

E 131 Terminology Relating to Molecular Spectrometry³

3. Terminology

3.1 Definitions:

3.1.1 For definitions of terms used in this test method, refer to Terminologies D 1129 and E 131.

3.1.2 For terms not defined in this test method or in Terminology D 1129 or E 131, reference may be made to other published glossaries.⁴

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 aliquot is pipetted into a pretreated glass vial. Concentrated HNO₃ and hydrogen peroxide are added and the sample heated to near dryness. This step is repeated as necessary and the residue is dissolved in dilute HNO₃. A complexant is added to an aliquot of this sample and analyzed in the phosphorimeter.

4.3 For screening purposes only, an aliquot of the sample may be pipetted directly into the phosphorimeter cell 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 emit luminescence of varying lifetimes after excitation. An advantage of 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).

¹ This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.04 on Methods of Radiochemical Analysis.

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² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 03.06.

⁴ 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.

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, and polyphosphates (Fluran,⁵ and Uraplex⁶).

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

6.6 If the concentration of uranium in the samples is high enough so that they can be diluted 1/100 with the appropriate nitric acid matrix, then interferences are reduced by diluting their effect.

7. Apparatus

7.1 *Laser Phosphorimeter*,⁷ meeting the following criteria:

7.1.1 *Detection Limit*—The detectable level for uranium must be 0.05 ng/mL 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 must be within 15 % relative standard deviation (R.S.D.).

7.2 *Labware*—If samples containing less than 0.1 ppb uranium are to be analyzed, digestion vessels (both TFE-fluorocarbon and glassware) if used, and liquid scintillation vials should be leached in hot nitric acid (1 + 3) 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.^{8,9} 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 D 1193, Type III.

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).

⁵ Fluran, available from Scintrex, DMW Geophysical Services, 2558 E. Montebellow, Sandy, UT 84092, has been found satisfactory for this purpose.

⁶ Uraplex, available from Chemchek Instruments, Inc., 1845 Terminal Drive, Richland, WA 99352, has been found suitable for this purpose.

⁷ Instruments, available from Chemchek Instruments, Inc., 1845 Terminal drive, Richland, WA 99352, and Scintrex, DMW Geophysical Services, 2558 E. Montebellow, Sandy, UT 84092, have been found suitable for this purpose. Consult appropriate equipment manuals for explanations of calibration and calculations.

⁸ *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 *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the United States Pharmacopeia and National Formulary, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

⁹ Supporting data available from ASTM Headquarters. Request RR:D-19-1148.

8.5 *Nitric Acid (1 + 3)*—Add one volume of concentrated nitric acid (HNO₃) to 3 volumes of reagent water, Type 1. This solution is 4 μ.

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

8.6 *Uranium Complexant*—Phosphoric acid, Fluran,⁵ or Uraplex⁶ 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 1 + 19 HNO₃ matrix.

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

10. Procedure

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

10.2 Add 1 mL of concentrated HNO₃ and two to three drops of 30 % hydrogen peroxide.

10.3 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.

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

10.5 Add 1.0 mL of HNO₃(1 + 3) and warm gently, if necessary, to dissolve the residue. Then add 4.0 mL of water conforming to Specification D 1193, Type I. Swirl to mix thoroughly.

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

NOTE 3—If the concentration of uranium in the prepared sample is high such that it is out of range of the calibrations, dilutions should be made using HNO₃(1 + 19), which is the concentration of nitric acid in the final sample preparation.

11. Calculation

11.1 Refer to the instrument manual for explanation of calculations.

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

11.3 Estimate the minimum detectable concentration by multiplying the standard deviation of replicate reagent blank analyses by 4.65.

12. Precision and Bias

12.1 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 D 2777.

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

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

12.4 The overall and single operator precision have been found to vary with level according to Table 2.

13. Quality Control

13.1 Whenever possible, the project leader, as part of the external quality control program, should submit quality control samples to the analyst along with routine samples in such a

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

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

way that the analyst does not know which of the samples are the quality control samples. These external quality control samples which usually include duplicate and blank samples, should test sample collection and preparation as well as sample analysis whenever this is possible. In addition, analysts are expected to run internal quality control samples that will indicate to them whether the analytical procedures are in control. Both the external and internal quality control samples should be prepared in such a way as to duplicate the chemical matrix of the routine samples, insofar as this is practical. The quality control samples that are routinely used consist of five basic types: blank samples, replicate samples, reference materials, control samples, and spiked samples.

14. Keywords

14.1 laser; phosphorescence; phosphorimetry; uranium; water

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