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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Method for Uranium Analysis in Natural and Waste Water by X-ray Fluorescence[1]

1. Scope

1.1 This test method applies for the determination of trace uranium content in natural and waste water. It covers concentrations of U between 0.05 mg/L and 2 mg/L.

1.2 *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. Summary of Test Method

2.1 Uranyl cations are collected on ion exchange cellulose phosphate papers by circulating the water to be analysed through the paper with a peristaltic pump. After drying, the uranium is determined using X-ray fluorescence.

3. Significance and Use

3.1 Uranium production facilities must control trace uranium content in their waste waters as well as in nearby environmental waters.

3.2 Colorimetric and fluorimetric methods have been developed but require a tedious separation of interfering elements. Trace uranium can also be determined by ICP-MS but not all water matrices are adapted (for example, waters with high salt content). Direct X-ray fluorescence can be done on the liquid but with a detection limit of ~5 mg/L

3.3 X-ray fluorescence after collection of uranium offers the advantages to reach low detection limits (0.05 mg/L) and to avoid handling a liquid in the spectrometer.

4. Interferences

4.1 Uranium is collected on the paper by the precipitation of a uranyl phosphate complex at pH = 2.5. Other cations (for example, Pb, Bi, Sn, Zr, As,...) having a low phosphate solubility at low pH are also collected and will interfere only at large concentration (the maximum capacity of the paper is 8.5 μeq/cm^2). As an example, for a solution containing 1 mg/L of each Pb, Bi, Sn, Zr, and As, and 0.3 mg/L of uranium, a bias of 5 % was detected on the uranium content. See also 9.2.

4.2 Other elements such as Fe, Cu, Ni, Al, Cr ..., which have a higher phosphate solubility at low pH were found to have no effect even at concentration of 10 mg/L.

4.3 The excess of anions forming strong complexes with the uranyl cation can also bias the uranium determination. As an example, for a solution containing 100 mg/L of F (added as NaF) and 0.3 mg/L of uranium, a bias of 30 % was found on the uranium determination. On the contrary, anions forming weak uranyl complexes (such as SO_4^{2-}, Cl^-...) were seen to have no effect even at concentration of several g/L.

5. Apparatus

5.1 *Wavelength dispersive X-ray fluorescence spectrometer* equipped with a LiF (200) crystal, a molybdenum, tungsten or rhodium target tube and a scintillation detector.

NOTE 1—Energy dispersive instruments may be applicable.

5.2 *Peristaltic pump* capable of achieving a flow rate of 50 mL/min.

5.3 *A filtration apparatus* which comprises a filter holder, a 250 mL flask located on top of the filter, and a pipe on bottom of the filter connected to the peristaltic pump. The sample to be analyzed is poured in the flask, flows through the phosphate filter and the liquid collected on bottom is brought back to the flask through the peristaltic pump.

5.4 *Pipet*—0.2 mL, 1 mL, 5 mL, 10 mL, 20 mL.[2]

5.5 *pH - meter*.

5.6 *100 mL volumetric flasks*.

6. Reagents and Materials

6.1 *Purity of Materials*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specification of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[3] Other grades may be used provided it is first ascertained that the reagent is of sufficiently

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[1] This test method is under the jurisdiction of ASTM Committee C-26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.05 on Methods of Test.

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[2] Dilution detailed in 6.5 and 6.7 may also be done by weight. In that case, pipets are not necessary.

[3] *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.

high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—Conventional distilled water is found acceptable for this analysis.

6.3 *Phosphate paper filters.*[4]

6.4 *Concentrated hydrochloric acid*, 12.1 *M* (sp gr 1.187).

6.5 *Diluted hydrochloric acid*, 5 *M*. Add 41 mL of concentrated hydrochloric acid (sp gr 1.187) to 50 mL H_2O in a 100 mL flask. Dilute to 100 mL with water.

6.6 *Ammonium chloride solution*, 2 *M*. Add 10.7 g of ammonium chloride salt to a 100 mL flask. Dilute to 100 mL with water.

6.7 *Diluted nitric acid*, 6 *M*. Add 37 mL of concentrated nitric acid (sp gr 1.42) to 50 mL H_2O in a 100 mL flask. Dilute to 100 mL with water.

6.8 *Uranium standard solution*, 10 g/L. This solution can be prepared by weighing 11.344 g of certified UO_2 (for example, OU 1 from CETAMA[5] with certified uranium content 88.12 ± 0.09 %), or equivalent, and adding 10 mL diluted nitric acid (6.7). After dissolution, dilute to 1 L with distilled water.

6.8.1 Uranium standard solution, 10 mg/L, obtained by dilution of solution 6.8.

7. Calibration and Standardization

7.1 Calibration an be done either in pure water as described here or, if an interference is suspected, in the matrix to be analysed using spikes. In seven 100 mL volumetric flasks, add respectively 0, 1, 2, 5, 10, 15, and 20 mL of solution 6.8.1. Dilute to 100 mL with distilled water. The uranium contration is respectively 0, 0.1, 0.2, 0.5, 1.0, 1.5 and 2.0 mg/L.

7.2 For each of the seven solutions (7.1), proceed as follows:

7.2.1 Adjust the pH of the solution to 2.5 ± 0.2 with concentrated HCl (6.4). The solution volume will then be slightly above 100 mL but will be refered as such for simplification purposes.

7.2.2 Just before the analysis, the phosphate paper must be converted to the ammonium form: insert a P 81 filter in the filter holder and start the peristaltic pump with a flow rate of 50 mL/min. Position the drain line so that the conditioning solution is not returned to the 250 mL flask. Add 50 mL of DI water to the 250 mL flask. When this has been pulled through the filter, add 100 mL of the dilute HCl (6.5). When complete add 100 mL of the ammonium chloride solution (6.6). The filter is then ready for collecting uranyl ions and should not dry in between.

7.2.3 Position the drain line so that sample solution is returned to the 250 mL flask. Pour the 100 mL solution (7.2.1) in the 250 mL flask. Let it flow for 1.5 h.

7.2.4 Recover the filter and let it dry at 50° C for 1 h.

7.3 Place the seven filters in the spectrometer holder, and analyze each by X rays at the uranium Lα peak, according to manufacturer's recommendations to achieve the user's performance and quality assurance criteria.

7.4 Calibrate the spectrometer with the seven standards. When plotting the X rays fluorescence intensity versus the concentration, a linear curve should be obtained.

8. Procedure

8.1 Measure out 100 mL of sample and proceed with the analysis as in 7.2 and 7.3.

NOTE 2—If the solution contains solids (precipitate, organic materials) a preliminary filtration should be done after step 7.2.1 but before step 7.2.3. A verification that all uranium has been dissolved after adjusting the pH at 2.5 is recommended.

NOTE 3—If the solution contains a lot of salts, or if 100 mL are not available, a dilution might be necessary prior to step 7.2.1. A correction factor is then taken in account.

8.2 Obtain directly the uranium concentration from the calibration curve obtained in 7.4.

9. Precision and Bias

9.1 *Precision*—For a sample containing 0.30 mg/L of uranium, 15 analyses have been performed to assess the short-term variability. The estimated relative standard deviation was found 2 % relative. The long term variability has been calculated over a four–month period (40 analyses), without recalibration, for a solution containing 0.1 mg/L uranium. The analyses were performed by two operators in one facility. The estimated relative standard deviation was found 15 % relative.

9.2 *Bias*:

9.2.1 *Uranium Recovery Rate on the Phosphate Paper*—The recovery rate was calculated by comparing a direct calibration of the X ray spectrometer and the analysis as described in Section 7. Direct calibration of the spectrometer was performed by depositing uranium on thin films and analyzing as in 7.3 and 7.4. On the other hand, a waste water sample was spiked with various uranium concentrations and analyzed according to 7.1-7.4. Table 1 shows the obtained results using the direct calibration. The recovery rate calculated from the four last spikes was found to be above 90 %.

9.2.2 *Interferences*—Bias can be checked when comparing calibration in pure water and calibration directly in the matrix. See Section 4 for examples of potential interferences.

10. Keywords

10.1 uranium; waste water; x-ray fluorescence

TABLE 1

Uranium added in waste water	Measured fluorescence intensity (kCp/s) Baseline is substracted	Concentration measured using direct calibration
0 mg/L	0.359	0.27 mg/L
0.1 mg/L	0.444	0.35 mg/L
0.2 mg/L	0.567	0.46 mg/L
0.5 mg/L	0.805	0.69 mg/L
0.8 mg/L	1.144	0.98 mg/L
1.0 mg/L	1.379	1.19 mg/L

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[4] A P81 Whatman filter has been found satisfactory.

[5] CEA/CETAMA, BP 171 30 207 Bagnols sur Ceze. France.