Lumex Instruments
Analytical Equipment

WATER QUALITY. METHOD FOR THE DETERMINATION OF MASS CONCENTRATION OF URANIUM IN SAMPLES OF NATURAL, DRINKING AND WASTE WATER USING LIQUID ANALYZER “FLUORAT-02-4M”

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WARNING — This Method does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

Tests conducted according to this document shall be carried out by suitably trained staff.

1 SCOPE

This document specifies a method for the determination of uranium mass concentration in samples of drinking, natural and waste water using “Fluorat-02” analyzer in the concentration range from 2 to 1000 μg/l.

Number of parallel determinations is two. Duration of a single determination is not more than 10 minutes.

2 PRINCIPLE

Luminescent method for the determination of uranium implies measurement of phosphorescence intensity of uranyl-ions (λ=530 nm) excited by ultraviolet radiation. In order to remove interfering influence caused by fluorescence, the photons counting mode of the analyzer combined with measurement of luminescence within a specified time window after the excitation impulse is employed. To enhance luminescence intensity, sodium polysilicate (pH=8-10) is added to the sample.

3 INTERFERENCES

To reduce concentration quenching of luminescence, samples of higher concentration are to be diluted. The influence of the sample matrix is excluded by the use of the standard additives method.

4 APPARATUS AND MATERIALS

4.1 **“Fluorat-02-4M” liquid analyzer** equipped with optical filters No 1 and 8

4.2 **Balance**, accuracy ± 0.1 mg

4.3 **Graduated volumetric pipettes**, nominal volume 1, 2 and 5 ml

4.4 **Glass volumetric flasks** with ground glass stopper, nominal volume 100 ml

4.5 **Volumetric cylinders**, nominal volume 100 ml

4.6 **Glass beakers**, nominal volume 25 and 50 ml

4.7 **Micropipette**, volume 200 - 1000 μl or 10 - 1000 μl

4.8 **Teflon vessels with screwed stoppers,** nominal volume 100 and 200 ml

4.9 **Teflon flasks**, nominal volume 100 ml

4.10 **Teflon or polypropylene vials**, nominal volume 10 ml

4.11 **Paper filters**, slow filtering or membrane filter, pore size 0.45 μm

4.12 **Electric hotplate with a closed heater**

Refer to ANNEX A for the method of labware cleaning.

5 REAGENTS

5.1 **Bidistilled or deionized water** (hereinafter - reagent water) complying with grade 1 requirements as defined in ISO 3696.

5.2 **Uranium ion standard solution** in diluted nitric acid, e.g. Sigma-Aldrich Uranium atomic absorption standard solution (1000 µg/ml U in 1 wt. % HNO_3). Use of metallic uranium or uranium nitrate hexahydrate is also possible (ref.6.2.1, 6.2.2).

5.3 Nitric acid, p.a. grade

5.4 Sodium hydroxide, p.a. grade

5.5 Colloidal Silicon Dioxide (CAS No 112945-52-5), p.a. grade (hereinafter referred as silicon dioxide)

6 SOLUTIONS

6.1 Nitric acid solution, $c(HNO_3) = 0.1$ mol/l

Dilute 7 ml of concentrated nitric acid up to 1000 ml with reagent water. Storage time is not limited.

6.2 Uranium stock solution of mass concentration 1 mg/ml

Prepare the stock solution of uranium by appropriate dilution of uranium standard solution. Storage time is 3 months.

If a uranium standard solution is unavailable, prepare the stock solution by either procedure.

6.2.1 From metallic uranium

Put 0.1000 g of metallic uranium into a 50 ml beaker and dissolve it in 5 to 10 ml of concentrated nitric acid. Evaporate it to wet salts and add 5 to 10 ml of nitric acid solution (6.1). On completion of dissolution, transfer solution into a 100 ml volumetric flask. Dilute it up to the mark with the same solution of nitric acid.

6.2.2 From uranyl nitrate hexahydrate

Dissolve 0.2110 g of uranyl nitrate hexahydrate in small amount of nitric acid solution (6.1) in a 100 ml volumetric flask and dilute it up to the mark with the same solution of nitric acid.

6.3 Uranium solutions of mass concentrations 2; 10; 100; 1000 μg/l for instrument calibration

Prepare these solutions on the day of use by sequential dilution of standard and/or stock uranium solution with nitric acid solution (6.1). Dilution uncertainty shall not exceed 2%.

Intermediate solutions of mass concentration 100 and 10 mg/l are stable up to 6 months.

Note 1 - If a new portion of nitric acid solution (6.1) was prepared, prepare new calibration solutions using it.

Note 2 - Storage time for calibration solutions (including 2 μg/l) can be prolonged by observing of cleanness, which is mainly defined by the purity of reagents used.

6.4 Preparation of sodium polysilicate solution

Put 5.0 g of sodium hydroxide in a 200 ml Teflon vessel, dissolve it in 100 ml of reagent water and add 14.3 g of silicon dioxide. Mark the liquid level on the outer surface of the vessel and close the vessel with a stopper but not tightly.

Heat the vessel content up to a slight boiling or simmering. Continue heating until complete dissolution of silicon dioxide, but not more, than during 8 hours adding from time to time reagent water up to the mark, if necessary.

Let the mixture settle and decant it off the residual if any into a 100 ml Teflon beaker with a screwed stopper or into a Teflon flask. Close tightly by a stopper.

Storage time is no longer than 1 month.

Do not store the solution in glass vessels. Once any residual appears, a new solution should be prepared.

Note 1 - Limitation of storage time of sodium polysilicate solution should be mainly attributed to the reaction with carbon dioxide from the atmospheric air. Therefore, transfer a small portion of it into an intermediate vessel before use. Close vessels with sodium polysilicate tightly and do not open them while not in use. Storage period for polysilicate solution in the basal vessel increases up to several months with accurate operation.

Note 2 - It is desirable to use fresh granular alkaline for preparation of polysilicate solution. This alkaline shall be stored in tightly closed vessels to eliminate absorption of carbon dioxide from the atmosphere.

NOTE 3 – The Teflon vessel is allowed to be heated on an electric hotplate with a closed heater. Heating of the vessel bottom above 200° C should be excluded.

7 SAMPLING

Sample volume shall be not less than 100 ml.

Preserve samples by adding of concentrated nitric acid on basis of 7 ml per 1 l of a sample. Storage time for preserved sample is 1 month.

To remove suspended matter, filter 5 to 20 ml of the preserved water sample through a paper filter. Separation of suspended matter by centrifugation is also possible.

Because of losses of uranium do not filter samples without addition of nitric acid.

8 INSTRUMENT SETUP

Prepare the analyzer for operation according to Operating manual. Make sure that optical filter No 1 is positioned in the excitation channel and optical filter No 8 is positioned in the registration channel.

When operating with FLUORATE software, consult relevant User's manual.

When operating without PC, proceed as follows.

If the **"Uranium"** item already exists in the **"List of substances"**, omit procedures described in this clause and come over to clause 9.

If there is no **"Uranium"** item in the **"List of substances"**, create it and thus appropriate sub-menus. Refer to User's manual for guidance. Recommended parameters are given below.

Method	**«Phosphorescence»**
Strobe delay	**300 μsec**
Strobe duration	**400 μsec**
PMT Sensitivity	**«2»**
Correct	**Full**
Calibr.	**PLA up**

9 MEASUREMENTS

9.1 General rules

The following rules shall be observed during background recording, instrument calibration and measurements.

9.1.1 When you place a cell into the cell compartment, an expose of photomultiplier to light usually occurs resulting in instability of readings within about 2 minutes (as a rule, they drop down). Therefore the cell compartment shall be closed immediately after you have inserted the cell in it. Start measurements until instrument readings stop significantly changing (for criteria, see below). From this point on, perform not less than five measurements and calculate the average value. Deviation of the results from their average value shall not exceed:

- in the **"Calibration"** mode:
  - ✓ 20% - for background measurement (J0);
  - ✓ 10% - for J1 measurements;
- in the **"Measurement"** mode:
  - ✓ 10% - for the 10 – 1000 μg/l concentration range;
  - ✓ 20% - for the lower concentrations.

9.1.2 Place the cells always similarly, e.g. with the mark facing the front panel of the instrument. One and the same cell shall be used for determination of background and uranium concentration below 10 μg/ml. It is desirable to use a separate cell for calibration and determination of concentration above 100 μg/ml.

9.1.3 Before measurements the cell shall be washed out with reagent water several times, then two times with 1 – 1.5 ml of the solution to be analyzed. After measurements, cell content shall be immediately poured out and the cell shall be, five times as minimum, washed out with reagent water.

WARNING - Polysilicate remains quickly destroy optical surfaces of the cell.

9.2 Calibration

9.2.1 Operation without PC

9.2.1.1 Calibration procedure

Place 5 ml of reagent water into a Teflon or polypropylene vial, add 0.5 ml of nitric acid solution (6.1), 0.5 ml of sodium polysilicate solution (6.4). Mix solution and place it into a cell of the analyzer.

Enter “Calibration” menu, set “C0” = 0.0000 and determine the value for “J0”. Calculate the average for five successive values. Press the ENT button. If the obtained value differs from the average value for not more than 20%, move cursor on to J1 row of the calibration table. If the deviation is larger, repeat the measurement.

Place 5 ml of reagent water into another vial, add 0.5 ml of uranium calibration solution of mass concentration 100 μg/l and 0.5 ml of sodium polysilicate solution (6.4). Mix solution and place it into a cell of analyzer.

Set C1=100 (uranium concentration in μg/l) and measure the value for “J1”. After determination of the average value for five successive measurements, enter it into the memory of device by means of a keyboard. You can also store the last value, if it differs from the average value not more than by 10%.

9.2.1.2 Verification of measurement range

Place 5 ml of reagent water into a vial, pipette 0.5 ml of the uranium calibration solution with concentration of 1000 μg/l and 0.5 ml of sodium polysilicate solution (6.4). Mix the solution, place it into a cell of the analyzer and measure uranium concentration in this solution in the “Measurement” mode.

Average value of five readings shall not differ from the rating value by more than 10%. If the obtained value is too low, samples shall be diluted in such a way that the values under determination (including the spike, ref. subclause 9.4) shall not exceed 200 μg/l.

It is admitted to use a multipoint calibration by including data for the solution of mass concentration 1000 μg/l to the calibration function obtained according to 9.2.1.1. Set C2= 1000 in the calibration table and get “J2” value as described in 9.2.1.1.

To check the performance of this multipoint calibration, perform measurement of uranium concentration for the solution with concentration 1 mg/l (1000 μg/l) in the “Measurement” mode. The obtained value shall not differ (as a rule, be greater) from the rating value for more than by 10%. If the excess is more, it is recommended to dilute samples if the concentration exceeds the limit of 200 μg/l.

9.2.2 Operation using FLUORATE software

To create a calibration, prepare calibration samples from reagent water and 3 - 4 calibration solutions (ref.6.3) in the range of 2 – 1000 μg/l or a part of it as follows.

Place 5 ml of reagent water into Teflon or polypropylene vial, add 0.5 ml of nitric acid solution (6.1), 0.5 ml of sodium polysilicate solution (6.4). Mix solution and place it into a cell of the analyzer. Use this calibration sample as a calibration blank.

Place 5 ml of reagent water into Teflon or polypropylene vial, pipette 0.5 ml of a respective uranium calibration solution and 0.5 ml of sodium polysilicate solution (6.4) into this vial. Mix the solution, place it into a cell of the analyzer and start measurements.

Select all the calibration points and create the calibration graph. Check for outliers using 10% criteria as tolerable deviation in the range of 10 to 1000 μg/l and 20 % below it.

Note 1 - Other uranium calibration solutions from the range of 2 – 1000 mg/l may be used.

Note 2 - Once a calibration sample is prepared, carry out the measurements. Do not prepare the next calibration sample until the measurements of the previous one are completed.

9.3 Quality assurance (QA test)

Place 5 ml of reagent water in a vial, pipette 0.5 ml of the QA test solutions with concentration of uranium in the range of interest and 0,5 ml of sodium polysilicate solution (6.4). Mix solutions and determine uranium concentration in the “Measurement” mode.

The calibration function is considered to be stable and acceptable if the relative difference of the measured concentration in the control solution and its actual concentration is less than 20% in the range of 2 - 10 μg/l or not more than 10% at the higher concentrations. If these requirements are not met, make sure that QA sample is prepared properly and repeat the procedure.

Calibration should be repeated again in the following cases:

- When stability test fails;
- After instrument repair.

9.4 Determination of uranium concentration in samples

Place 5 ml of reagent water into a vial, pipette 0.5 ml of the sample prepared according to clause 7 and 0.5 ml of sodium polysilicate solution (6.4). Mix solution and place it into a cell of analyzer. Determine uranium concentration in the “Measurement” mode according to requirements of 9.1.

Prepare the sample spiked with uranium. For this, add 1 ml of uranium solution with concentration by 5 – 15 times exceeding the determined concentration to 10 ml of sample and calculate concentration of the additive to the sample (C_{add}, μg/l):

$$C_{add} = C_c \cdot \frac{V_c}{V_o + V_c}, \qquad (1)$$

where C_c is the mass concentration of uranium in the solution used for spiking, μg/l;

V_c is the volume of the uranium solution used for spiking, ml;

V_0 is the initial volume of the sample to which the uranium solution was added, ml.

Place 5 ml of reagent water into another vial, pipette 0.5 ml of spiked sample and 0.5 ml of sodium polysilicate solution (6.4). Mix solution and place it into a cell of analyzer. Determine uranium concentration in the “Measurement” mode.

10 CALCULATION

Calculate the mass concentration of uranium concentrations in the sample as follows:

Calculate the average arithmetical value of the measured concentrations for both the initial sample and the sample spiked with uranium.

Calculate uranium concentration (X, μg/l) using equation (2):

$$X = \frac{X_s \cdot C_{add}}{X_{add} - X_s}, \qquad (2)$$

where X_s is the averaged mass concentration of uranium in the sample, μg/l;

X_{add} is the measured concentration of uranium in the sample spiked with uranium, μg/l;

C_{add} see equation (1), μg/l.

If quenching effects do not exceed 25%, i.e.

$$| X_{add} - X_S - C_{add} | < 0{,}25 \cdot C_{add}, \qquad (3)$$

it is admitted to accept Xs as the measurement result.

Report the average arithmetical mean of two parallel results as the result of measurement given the difference between them do not exceed the limit of repeatability set in the laboratory. Consult ISO 5725-1 and ISO 5725-6 for further guidance.

11 EXPRESSION OF RESULTS

Report the results in μg/l and round them to not more than two digits. Examples:

Uranium	5.4 μg/l
Uranium	75 μg/l

Uranium	240 μg/l

12 TEST REPORT

This clause specifies which information is to be included in the test report:

- a reference to this Method;
- complete identification of the sample;
- expression of results as indicated in Clause 11;
- sample pre-treatment if applicable;
- any deviations from this method and details of all circumstances which could have affected the result.

ANNEX A

(informative)

LABWARE PREPARATION FOR ANALYSIS

Proper preparation and keeping clean labware intended for the determination of uranium is critical, so follow the rules below.

A.1 Use concentrated nitric acid only to wash the labware. Never use soda, all kinds of alkali and synthetic detergents or mixtures containing Cr(VI) compounds.

A.2 Preliminary wash the labware with tap water, pour the acid into the vessel being cleaned, thoroughly bathe the inner surface of it and pour the acid out into a special vessel. Fill up the pipettes several times with the acid above the mark. Rinse the labware with distilled water at least 5 times. Finally, rinse it with the reagent water (2-3 times).

A.3 It is recommended to have a special set of labware for the determination of uranium only.

A.4 **TO PREVENT IRREVERSIBLE DESTRUCTION OF THE OPTICAL SURFACE** wash out the cell directly on measurements completion. Never leave the cell filled with solutions or drops of them for more than 2 - 3 minutes.

A.5 Avoid taking reagents for analysis (water, nitric acid, polysilicate solution and calibration solutions) from vessels where they are stored and use marked intermediate vessels. Being filled, these vessels should be firmly closed. Never pour reagents from intermediate vessels back into vessels where they are stored. With such operation practice, storage period for calibration solutions even with low concentrations of uranium is limited by availability of the portion of nitric acid (0.1 mol/l) used for preparation of these solutions.

A.6 Do not touch walls of vials with tips of pipettes, especially dispensing polysilicate solution.