

Chemical toxicity of uranium. Determination of uranium concentration in water by means of fluorescence

1. This is the formal instruction «Method for the determination of mass concentration of uranium in the samples of natural, drinking and waste water with the use of liquid analyzer “Fluorat-02-2M”». The guideline to this laboratory work is performed according with this instruction.

2. The procedure is assigned for the determination of uranium mass concentration in samples of drinking, natural and waste water with the use of “Fluorat-02” analyzer in the concentration range from 2 to 1000 mg/l. Number of parallel determinations is two. Duration of a single determination is not more than 10 minutes.

3. Luminescent method for the determination of uranium implies measurement of delayed fluorescence intensity of uranyl-ions ($\lambda=530$ 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 poly-silicate (pH=8-10) is added to the sample.

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. Necessary apparatus and materials:

- “Fluorat-02-2M” liquid analyzer equipped with optical filters No 1 and 8
- Balance, accuracy ± 0.1 mg
- Graduated volumetric pipettes, nominal volume 1, 2 and 5 ml
- Glass volumetric flasks with ground glass stopper, nominal volume 100 ml
- Volumetric cylinders, nominal volume 100 ml
- Glass beakers, nominal volume 25 and 50 ml
- Pipette dispensers, nominal volume 0.5 and 1 ml
- Teflon vessels with screwed stoppers, nominal volume 100 and 200 ml
- Teflon flasks, nominal volume 100 ml
- Teflon or polyethylene vials, nominal volume 10 ml
- Paper filters, slow filtering

5. Necessary reagents

- Reagent water complying with grade 1 as defined in ISO 3696 (as usual bidistilled or deionized water)

- Uranium ion standard solution of mass concentration e.g. 300 mg/l

- Nitric acid, p.a. grade

- Sodium hydroxide, p.a. grade

- Amorphous silica, p.a. grade

6. Solutions preparation

6.1 Nitric acid solution, $c(\text{HNO}_3) = 0.1 \text{ mol/l}$

Dilute 7 ml of concentrated nitric acid up to 1000 ml with reagent water. Storage time is unlimited.

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.

6.3 Uranium solutions of mass concentrations 2; 10; 100; 1000; 2000 mg/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 2 weeks.

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

Note 2 - Storage time for calibration solutions (including 2 mg/l) can be prolonged by observing of cleanness is mainly defined by the absence of pollution of reagents used.

6.4 Preparation of sodium poly-silicate solution

Intermediate solutions of mass concentration 100 and 10 mg/l are stable up to 2 weeks.

Put 5.2 g of sodium hydroxide in a 200 ml Teflon vessel, dissolve it in 100 ml of reagent water and add 14 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 dilution of amorphous silica, 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 not 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 attributed mainly 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.

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. If the “**Uranium**” item already exists in the “**List of substances**”, omit procedures described in this clause and come over to clause 9. If you wish to check parameters set earlier, enter menu “**Parameters**” of the “**Uranium**” item as laid out below.

If there is no “**Uranium**” item in the “**List of substances**”, create it and thus appropriate sub-menus. Refer User’s manual for guidance. Some outlines are given below. Place cursor on “**Uranium**” item (that means on the appropriate line in the “**List of substances**”) and press the ENT button to enter the “**Selection of the measurement method**” menu. Place cursor on the line with the name of the method (by default it is Luminescence) and press the ENT button to enter the “**Measurement methods**” menu. Select “**Phosphorescence**” as a measurement method, press the ENT button and preset the following parameters:

“**Strobe delay**” 300 msec

“**Strobe duration**” 400 msec

Press the ESC button to return to the “**Selection of the measurement method**” menu. Position the cursor at the “Parameters” line. Enter this menu and set parameters as follows:

“**Sensitivity**”- maximum

“**Corr. Ref.**” - yes

“Corr. Trans.”- yes

9 Measurements

9.1 General rules

The following rules shall be observed during background recording, instrument calibration and measurements. 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 mg/l concentration range;
 - _ 20% - for the lower concentrations.

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 mg/ml. It is desirable to use individual cell for calibration and determination of concentration above 100 mg/ml.

Before measurements the cell shall be washed out with bi-distillated water for several times, then two times with 1 – 1,5 ml of the solution to be analysed. After measurements, cell content shall be immediately poured out and the cell shall be, five times as minimum, washed out with bi-distillated water. Polysilicate remains quickly destroy optical surfaces of the cell.

9.2 Calibration

9.2.1 Place 5 ml of reagent water into Teflon or polyethylene 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 analyzer.

9.2.2 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%, save it and pass on to the next row of the calibration table. If the deviation is larger, repeat the measurement.

9.2.3 Place 5 ml of reagent water into another vial, add 0.5 ml of uranium calibration solution of mass concentration 0.1 mg/l and 0.5 ml of sodium polysilicate solution (6.4). Mix solution and

place it into a cell of analyzer.

9.2.4 Set C1=100 (uranium concentration in mg/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%.

9.3 Determination of uranium concentration in samples

Place 5 ml of reagent water into a vial, pipette 0.5 ml of 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 a sample of water with an additive. 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 (C_{add} , mg/l):

$$C_{add} = C_c \cdot \frac{V_c}{V_o + V_c},$$

where C_c is the mass concentration of uranium in the solution used as the additive, mg/l;

V_c is the volume of the uranium solution used as the additive, ml;

V_o 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 sample with an additive 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 with the additive.

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

$$X = \frac{X_s \cdot C_{add}}{X_{add} - X_s},$$

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

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

If quenching effects do not exceed 25%, it is admitted to accept X_s 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 mg/l and round them to not more than two digits. Examples:

Uranium 5.4 mg/l

Uranium 75 mg/l

Uranium 240 mg/l

12 Measurement uncertainty

Information on uncertainty evaluation conducted in the LUMEX Ltd laboratory yielded results given in Table 1.

Table 1 - Relative expanded uncertainty with the coverage factor $k = 2$

Measurement range, $\mu\text{g/l}$	$U_{rel} (k=2), \%$
Drinking water	
From 2 to 5 incl.	50
Over 5 to 50 incl.	36
Over 50 to 500 incl.	30
Over 500	20
Natural and waste water	
From 2 to 5 incl.	50
Over 5 to 100 incl.	40
Over 1000	30