भारतीय मानक
Indian Standard

IS 14194 (Part 3/Sec 1) : 2024

पर्यावरण नमूनों में रेडियोन्यूक्लाइड — आंकलन की पद्धतियाँ

भाग 3 यूरेनियम

अनुभाग 1 पानी के नमूने में

(दूसरा पुनरीक्षण)

Radionuclides in Environmental Samples — Methods of Estimation

Part 3 Uranium

Section 1 In Water Sample

(Second Revision)

ICS 13.020.40; 13.280

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March 2024 **Price Group 6**

Nuclear Energy for Peaceful Application Sectional Committee, CHD 30

FOREWORD

This Indian Standard (Part 3/Sec 1) (Second Revision) was adopted by the Bureau of Indian Standards, after the draft finalized by the Nuclear Energy for Peaceful Applications Sectional Committee, had been approved by the Chemical Division Council.

Radioactivity from several naturally occurring and anthropogenic sources is present throughout the environment. Uranium, radium, strontium (^{90}Sr), iodine (^{131}I) and caesium (^{137}Cs) are the radionuclides of importance in environmental radioactivity monitoring. Uranium occurs in natural waters as a composite of three isotopes (^{234}U, ^{235}U and ^{238}U) at low specific activity of ppb (µg/l) or sub-ppb levels. Except uranium, other radionuclides in environmental samples are evaluated by separation and the radioactivity is measured by either of alpha, beta or gamma radiation, emitted by the radionuclides.

This standard was first published in 1994 for measurement of uranium by fluorimetric method, which is very sensitive compared to radiation measurement. In the first revision in 2021, terminology given in the standard was modified to align them with the terminology given in other parts of IS 14194. Alternate method for preparation of water sample was also prescribed.

While reviewing this standard, the committee has decided to further divide this standard into two sections, one for only water sample and other for geological and biological samples for the purpose of better understanding and clarity. This section covers the measurement of uranium in water sample (for example, surface water, ground water and sea water). IS 14194 (Part 3/Sec 2) covers uranium measurement in geological and biological samples like soil, sediment, rock, vegetation, food and biota samples.

All laboratories shall be duly certified by Atomic Energy Regulatory Board, Government of India for carrying out analysis or measurement of radioactivity in commodities.

The composition of the Committee responsible for the formulation of this standard is given in Annex B.

In reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 2022 'Rules for rounding off numerical values (*second revision*)'.

Indian Standard

RADIONUCLIDES IN ENVIRONMENTAL SAMPLES — METHODS OF ESTIMATION

PART 3 URANIUM

SECTION 1 IN WATER SAMPLE

(Second Revision)

1 SCOPE

The method described in this standard uses light-emitting diode (LED) fluorimetry to estimate the total uranium content of water sample.

2 REFERENCES

The standard given below contain provisions which, through reference in this text, constitute provisions of this standard. At the time of publication, the edition indicated was valid. All standards are subject to revisions, and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent edition of this standard:

IS No.	*Title*
IS 1070 : 2023	Reagent grade water — Specification (*fourth revision*)

3 TERMINOLOGY

3.1 Activity

The number of spontaneous nuclear disintegrations occurring in a certain quantity (weight/volume) of material during a specified time interval, divided by that time interval. It is expressed in Becquerel (Bq), where 1 Bq = 1 disintegration/ second. Earlier unit of activity was Curie (Ci), where $1 \text{ Ci} = 3.7 \times 10^{10}$ disintegrations/second.

3.2 Radionuclide

An element, with a certain mass number and atomic number, which undergoes spontaneous disintegration in a measurable period of time.

4 PRINCIPLE

Uranium present in a sample forms a complex with sodium-pyrophosphate, a fluorescence enhancing agent, in a 9 ml suprasil quartz cuvette. This complex is excited by LED at an excitation wavelength of 410 nm from an array of LEDs (7 numbers). The uranium complex, then fluoresces with emission peaks at 494 nm, 516 nm, 540 nm and 565 nm, with maximum at ~ 510 nm. The fluorescent radiation is detected by a photomultiplier tube (PMT). The detector is present at right angle to the radiation source, thus the background signal due to the source will be negligible and a lower detection level can be achieved than atomic absorption or emission techniques.

The fluorescence of organic matters excited by the nitrogen laser have very short lifetime (< 100 ns) compared to that of uranyl complex (~ 200 µs). By measuring the delayed fluorescence signal (only for a 100 µs period starting from 30 µs after the laser pulse) and fluorescence signals from the PMT are integrated for 4 s and then displayed. Thus, the fluorescence due to organic compounds dies down and only the fluorescence of uranium isotopes collected by the time gated PMT. The fluorescence is proportional to concentration of uranium in aqueous medium.

Otherwise, the fluorescence peak of organic matters is around 400 nm and that of uranium in complexing media are 494 nm, 516 nm, 540 nm and 565 nm, maximum around 510 nm. Therefore, using an optical filter at 450 nm, the contribution of organic matters is nullified. Thus, the fluorescence interference due to organic matters is corrected by using proper optical filter, fixed electronic delay and gating technology. The quenching effect encountered due to the presence of high concentration of acid (up to 2 M) during analysis, is removed by a proper *p*H adjustment prior to analysis.

5 APPARATUS

5.1 LED Uranium Fluorimeter

The total uranium content in the water samples is analysed using a uranium fluorimeter system. It is a compact analytical instrument based on fluorimetric technique and micro-optics. The instrument contains LED/laser source, sample compartment and a PMT placed in right-angle optical configuration. The fluorescence interference originating from organic matters and other metals in the samples, is corrected by optical filter, fixed electronic delay and gating. Uranium concentration in the samples can be estimated using the standard addition method, to avoid matrix effect. The working range and minimum detection level (MDL) of the instrument shall be 0.2 µg/l to 20 µg/l and 0.2 µg/l, respectively.

5.2 Micro-Pipettes — (5 ml, 0.5 ml, 100 µl, 50 µl) with disposable tips.

5.3 Analytical Weighting Balance

5.4 *p*H Meter

5.5 TDS Meter

5.6 Suprasil Quartz Cuvette with Teflon Cap

5.7 Lint Free Wipers

5.8 Uranium Standard Solution (100 ppm or Higher)

5.9 Sodium Pyrophosphate — purity more than 99 percent.

5.10 Phosphoric Acid — purity more than 90 percent.

6 REAGENTS

6.1 Stock Solution

A stock solution of 0.973 g/l uranium (Aldrich make) is diluted to working concentration using ultrapure water (*see* Note) for regular calibration of the system.

NOTE — Ultrapure water shall have specification given in Table 1.

Table 1 Requirement of Ultrapure water

(*Clause* 6.1)

Sl No. (1)	Parameter (2)	Requirement (3)
i)	Resistivity (25 °C)	> 18.18 MOhm
ii)	Total organic carbon (on-line for < 10 ppb)	< 1 µg/l
iii)	On-line dissolved oxygen	10 µg/l

6.2 Fluorescence Enhancing Agent — 5 percent sodium pyrophosphate (SPP).

Dissolve 1.25 g of sodium pyrophosphate (SPP) in 20 ml of ultrapure water and add drop-wise phosphoric acid to adjust *p*H ~ 7 and then make up the volume up to 25 ml using ultrapure water. Label the date of preparation and final *p*H of the solution on the standard flask.

NOTE — All the volumetric additions to be carried out using both micro-pipettes and analytical weighing balance to confirm amount by volumetry and gravimetry.

7 MEASUREMENT PROCEDURE

7.1 Switch on the instrument and allow it to warm-up and equilibrate with room temperature for one hour.

Calibrate the fluorimeter with four uranium standards of increasing concentrations to check the instrument performance and the linear dynamic range. For zero concentration, pipette out 5 ml of double distilled water onto a dry suprasil quartz cuvette and add 0.5 ml of buffer that is 5 percent SPP, mix well and record the system blank (B ± σ). Fig. 1 shows a typical calibration graph for fluorimeter response using standard uranium solutions. The water samples have to be filtered using 0.45 micron filter papers and a vacuum filtration assembly before analysis to remove the suspended solids. If the total dissolved solids (TDS) level is low (< 1 500 ppm), then the water sample can be directly analysed for uranium using fluorimeter, no chemical processing is required. The sample and standard are maintained at room temperature before analysis by the equipment in the same room. High TDS samples, like seawater, are treated in a separate manner, the details of processing of seawater samples are given in Annex A.

7.2 Pipette out 5 ml of water sample onto a cleaned and dry cuvette, add 0.5 ml of 5 percent SPP (buffer with *p*H ~ 7). Record the fluorescence response of the sample only, in terms of counts, minimum 4 readings.

7.3 Add 50 µl of 500 µg/l uranium standard, gravimetrically and volumetrically, onto the cuvette that contains the sample and buffer, record the fluorescence response after the first standard addition.

7.4 Repeat the above sequence, that is again add 50 µl of 500 µg/l uranium standard onto the cuvette and record the fluorescence response after second standard addition.

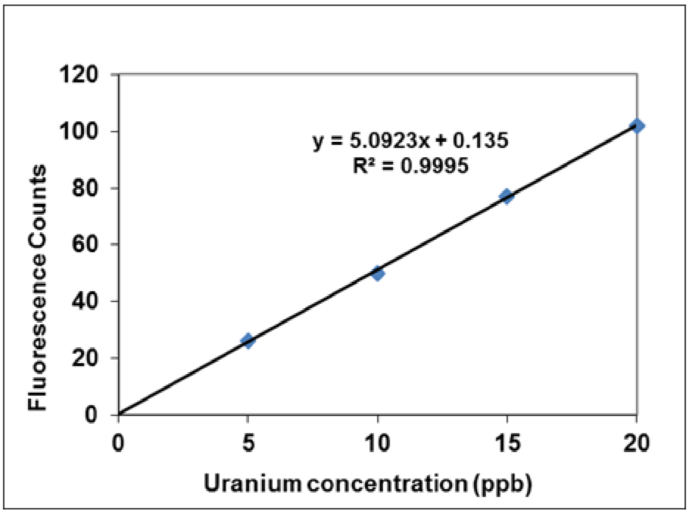

FIG. 1 CALIBRATION GRAPH FOR FLUORIMETER RESPONSE USING STANDARD URANIUM SOLUTION

7.5 The concentration of uranium (ppb or µg/l) in samples was calculated by using the formula,

Uranium concentration (ppb or µg/l) =

$$\frac{D_1}{(D_2 - D_1)} \times \frac{(V_2 \times \text{C})}{V_1}$$

where

D_1 = fluorescence due to sample only (blank subtracted);

D_2 = fluorescence due to sample and uranium standard (blank subtracted);

V_2 = volume of uranium standard (ml);

V_1 = volume of sample taken (ml); and

C = concentration of uranium standard (ppb or µg/l).

In case of multiple standard additions, the counts from **7.2**, **7.3**, and **7.4** steps above are populated in a table and then fluorescence data is plotted against concentration of uranium present in the sample after standard addition. From the slope of the graph, counts per µg/l are obtained. Dividing the net counts for sample (blank subtracted sample fluorescence) with the value of slope, uranium concentration in sample is calculated.

7.6 Error Propagation

Fluorescence count for the sample $S = S \pm \sigma_S$

Blank count for the instrument $B = B \pm \sigma_B$

Net count = $D \pm \sigma_D = (S - B) \pm (\sigma_S^2 + \sigma_B^2)$

where

$D = S - B$; and

$\sigma_D = (\sigma_S^2 + \sigma_B^2)$.

8 CALCULATION

8.1 In Absence of Matrix Effect (No Quenching)

This method is applicable for synthetic samples where concentrations of quench inducing elements are zero or negligible. To estimate uranium concentration in such samples, evaluate the calibration factor *F* (ppb/count or µg/l per count of uranium) from the slope of calibration curve.

Uranium concentration in ppb or µg/l in sample =

$$(S - B) \times F$$

where

S = fluorescence count for the sample; and

B = blank count for the instrument (only 5 ml distilled water and 0.5 ml SPP).

8.2 In Presence of Matrix Effect

Most of water samples are of natural origin, for example groundwater, surface water etc which contains different levels of TDS concentrations and may have unknown amount of elements contributing to quenching of uranium fluorescence. In this case standard addition method has to be followed to correct the matrix effect. Quenching due to matrix effect can be detected from sample counts and sample plus standard counts. If the latter is not nearly equal to the sum of counts of sample and standard measured separately, quenching is present. In such cases, standard addition method is followed.

Standard addition method involves analysing solutions containing the same amount of the sample to be analysed, but increasing amounts of standard being added. The uranium concentration in the sample is unknown but in the standard is known.

For example, 5 ml of unknown sample is first measured, then 0.05 ml of uranium standard is added to it before two successive measurements. The idea of this procedure is that the total uranium concentration is the sum of the uranium present in the unknown sample and known standard, and that the total uranium concentration varies linearly. If the signal response is linear in this concentration range, then a plot similar to Fig. 2 is generated.

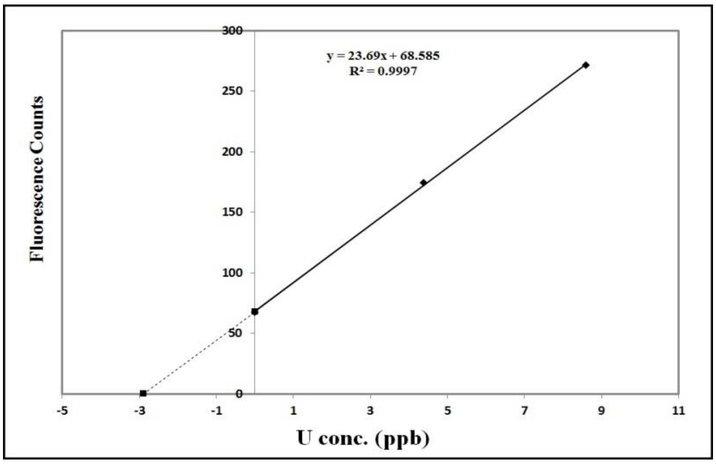

FIG. 2 STANDARD ADDITION GRAPH FOR UNKNOWN SAMPLE

9 QA/QC

9.1 Only Analytical Reagent (AR) grade chemicals and reagents to be used.

9.2 Ultrapure water to be used for preparation of stock standards and reagents.

9.3 Glassware to be used for sample processing and storage are to be soaked in 10 percent nitric acid followed by rinsing with ultrapure water before use, to prevent sorption of elements on the walls of the container.

9.4 Analyse duplicate samples, reagent/process blanks, analytical blanks and known standards during the process for quality control.

10 PRECAUTIONS

10.1 Effect of *p*H on Fluorimeter Response

The *p*H of the processed sample should be slightly acidic or neutral. The *p*H of the solution should not be too acidic. Also, highly acidic sample will hinder the complexation of uranium with the SPP. Alkaline *p*H must be avoided because iron and calcium will be precipitated and hence the chance of wall absorption leading to lower transparency of fluorescence photons. After addition of the buffer, the *p*H of the solution should be in the range of 6 to 7 for maximum fluorescence response.

10.2 Effect of TDS on Fluorimeter Response

Fig. 3 shows the effect of TDS on fluorimeter response. Most often high levels of TDS are caused by the presence of K, Cl, Na, etc. Beyond 1 500 ppm of TDS the fluorimetric response of the uranium analyser decreases due to decrease in transparency of sample to fluorimetric photons. Therefore, in case of high TDS content in the sample, precautions should be taken during measurement of uranium in water samples directly by fluorimetric techniques. The sample needs to be diluted accordingly and analysed to get proper fluorimetric response with respect to uranium concentration.

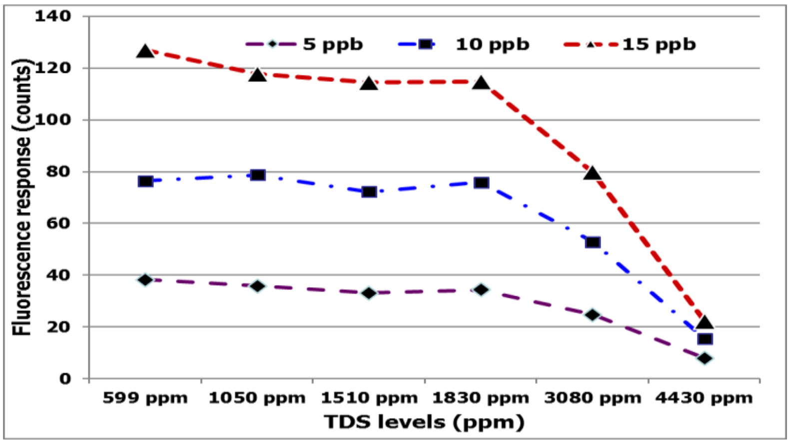

FIG. 3 EFFECT OF TDS ON LED FLUORIMETER RESPONSE

10.3 Effect of Temperature and Dust Free Environment

The method involves fluorescence emission and detection of emitted photons via photocathode of a photo-multiplier tube, both temperatures dependent. Hence the surrounding temperature should remain constant for a steady result. The laboratory should be dust free and the tissue papers used for swiping cuvette should be fiber free to avoid baffling scattering in the cuvette.

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ANNEX A

(*Clause* 7.1)

URANIUM ANALYSIS IN SEAWATER SAMPLES BY LED FLUORIMETRY

A-0 GENERAL

In sea water samples the interference due to high concentration of chloride ion decreases the uranyl fluorescence in the aqueous solution of the sample. The fluorescent response from a given uranium level is reduced by nearly 50 percent at 500 ppm chloride.

A-1 REAGENTS

A-1.1 $K_2S_2O_8$

A-1.2 10 N NaOH Solution

A-1.3 10 Percent HNO_3 Solution

A-3 PROCEDURE

A-3.1 Pipette 5 ml sample into a 150 ml beaker.

A-3.2 Add 1g to 2 g of $K_2S_2O_8$, followed by the addition of 20 ml of deionised water.

A-3.3 The solution is boiled to dryness in a hotplate (20 min to 30 min). White residue appears, then melts with evolution of white fumes.

A-3.4 Remove beaker from hot plate and add 40 ml of deionised water after cooling to room temperature.

A-3.5 Check *p*H after shaking well for dissolution. In case of detection of acidic *p*H, 2 to 3 drops of NaOH have to be added to make *p*H slightly basic (7 to 8), to ensure neutralization of excess persulfate.

A-3.6 Add few drops of 10 percent HNO_3 to make solution slightly acidic and the make-up volume up to 50 ml.

A-3.7 Cool the solution to room temperature.

A-3.8 Analyse by standard addition method.

A-4 PRECAUTION

No solids should be left when the neutralization is completed. Since the residue is primarily due to potassium bisulphate, failure to follow this precaution will result in low final *p*H and hence low response during analysis.

ANNEX B

(*Foreword*)

COMMITTEE COMPOSITION

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This Indian Standard has been developed from Doc No.: CHD 30 (21930).

Amendments Issued Since Publication

Amend No.	Date of Issue	Text Affected

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Published by BIS, New Delhi