

Reply to:

Uranium concentration in ground water samples belonging to some areas of Western Haryana, India using fission track registration technique

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Accepted 25th March, 2013

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Dear Editor,

I have read the above cited paper very carefully. The undersigned has been involved in the analysis of geological materials and hydro-geochemical reconnaissance surveys attached with mobile geochemical laboratories in different parts of India for uranium exploration activities of the Atomic Minerals Directorate for Exploration and Research. I have also contributed on uranium determination in diverse matrices vide my publications:

1. Rathore DPS, Kumar M, Tarafder PK (2012). Presentation of differential laser-induced fluorimetry as a reference measurement procedure for determination of total uranium content in ores and similar matrices. *Accred. Qual. Assur.* 17:75-84
2. Rathore DPS (2008). Advances in Technologies for the Measurement of Uranium in Diverse Matrices (Review article). *Talanta* 77:9-20.
3. Rathore DPS (2007). Trends in the Methods of Measurement in Analytical Chemistry. *Explor. Res. At. Miner.* 17:145-149.
4. Rathore DPS, Kumar M (2004). Analytical Applications of a Differential Technique in Laser-Induced Fluorimetry: Accurate and Precise Determination of Uranium in Concentrates and for Designing Microchemielectronic Devices for on-line Determination in Processing Industries. *Talanta* 62:343-349.
6. Tarafder PK, Kunkal L, Murugan P, Rathore DPS (2002). Ion-associate Solvent Extraction of Uranium with 2,3-Dihydroxynaphthalene and Cetyltrimethylammoniumbromide, and its fluorimetric Determination in Silicate Rocks. *Radioanal. Nucl. Chem.* 253:135-142.
7. Manjeet Kumar, Rathore DPS, Singh AK (2001). Quinalizarin Anchored on Amberlite XAD-2: A New Matrix for Solid-Phase Extraction of Metal Ions for Flame Atomic Absorption Spectrometric Determination. *Fresenius J. Anal. Chem.* 370:377-383.
8. Kumar M, Rathore DPS, Singh AK (2001). Pyrogallol Immobilized Amberlite XAD-2: A Newly Designed Collector for Enrichment of Metal Ions Prior to their Determination by Flame Atomic Absorption Spectrometry. *Mikrochimica Acta* 137:127-135.
9. Rathore DPS, Tarafder PK, Kayal M, Kumar M (2001). Application of a Differential Technique in Laser-Induced Fluorimetry: Simple and a Precise Method for the Direct Determination of Uranium in Mineralised Rocks at Percentage Level. *Anal. Chim. Acta* 434:201-208.
10. Kumar M, Rathore DPS, Singh AK (2000). Metal Ion Enrichment on Amberlite XAD-2 Functionalized with Tiron: Analytical Applications. *Analyst* 125:1221-1226.

Also, my three recent publications;

1. Rathore DPS (2013). Letter to the Editor: Query related to the publication titled, "Application of fission track technique for estimation of uranium concentration in drinking waters of Punjab" by Prabhu et al. 294:443–446 (2012), doi:10.1007/s10967-011-1503-2, J. Radioanal. Nucl. Chem. DOI 10.1007/s10967-013-2432-z
2. Rathore DPS (2013). Letter to Editor : Query related to publication titled "A comparative analysis of uranium in potable waters using laser fluorimetry and ICPMS techniques" by Shenoy et al. 294:413–417 (2012), doi: 10.1007/s10967-012-1705-2, J. Radioanal. Nucl. Chem. DOI 10.1007/s10967-013-2445-7.
3. Rathore DPS (2013). Letter to the Editor: Query related to publication titled "Study of uranium contamination of ground water in Punjab state in India using X-ray fluorescence technique" by Alrakabi et al. 294:221–227 (2012), doi:10.1007/s10967-011-1585-x, J. Radioanal. Nucl. Chem. (DOI) 10.1007/s10967-013-2449-3.

Based on my experiences gained so far, I would like to share some of my observations as follows:

1. There are three essential parameters for the reliability of measurement results for naturally occurring water samples:
 - a. Sampling: Water sample should be free from suspended matter/sediments. It should be filtered before collection and its preservation. For preservation of water samples, it should be acidified with AR nitric acid to pH-1.
 - b. Time interval between water collection and analysis. For un-acidified water samples, water sample should be analysed on the same day.
 - c. Methodology adopted for uranium analysis.

Complete and unequivocal preservation of samples, whether domestic waste or natural water is a practical impossibility. The physicochemical and biological changes continue inevitably after sample collection. This warrants the need and use of Mobile Geochemical Laboratory for on-the-spot/quick analysis of water samples.

Hydro-geochemical reconnaissance program for the exploration of uranium seems to be very simple in terms of sampling, analytical techniques, interpretation of data etc., when in fact; it is a difficult task if the elapsed time interval between sampling and analysis is more. It is due to the fact that the degree of variations in the contents of major cations and anions and uranium are in unpredictably significant manner as stated below, leading to erroneous results and their interpretations. The samples must not be contaminated with the elements to be determined and should not undergo physico-chemical changes which result in loss or increase of uranium and other elements. There is always a need of periodic self-evaluation of data, that is, from collecting samples to reporting results.

The water samples collected and sent for analysis should be a true water sample that is, free from suspended or particulate materials, properly stored or preserved so that it should be free from any variations in the content of water samples (IAEA, 1973; 1988; Robbins, 1978; APHA, 1980).

2. On page 353, MATERIALS AND METHODS section of the manuscript, both these essential parameters (A and B) of water sampling have not been stated in the manuscript. Hence to proceed further for analytical measurement is a waste of time and it has no meaning. Results and discussion based on such unreliable results will be highly misleading.

Changes in Uranium contents of samples: Uranium levels also changes considerably probably due to adsorption, co-precipitation etc. It is necessary that before acidification of water sample, it should be free from suspended particulate materials, if not, should be filtered; otherwise, uranium levels may not be a true value and may increase or decrease. A gain is presumed to occur when suspended particulate material with comparatively high uranium levels slowly equilibrates with the water. Losses probably occur due to the container walls. In general, for the preservation of samples for the determination of metal ions at trace levels, the water samples should be acidified after filtration only.

In addition, the presence of fluoride above 1.5 mg/l in water samples effects the variation in the contents of uranium in un-acidified samples to a greater extent with respect to time-interval between water sample collection and analysis. When the water sample is collected, the equilibrium between rocks and water is disturbed. With passage of time, fine colloidal suspension (particles) floats on the surface of the water sample in the container (probably calcium fluoride, CaF_2). As calcium fluoride is a very good co-precipitant of uranium, it adsorbs uranium from the whole sample volume. Therefore, when we analyse samples for uranium contents, these particles enriched in uranium shows high uranium contents which may not be a representative value/true value of uranium in samples. Fluoride

contents above 1.5 mg/l has been reported in this part of the country. In my opinion, actual value of uranium contents in such water samples (containing fluoride) should not be abnormally very high. With further passage of time, you will find deposition of salts in the bottom of the container [there is a well known method for: "Determination of ultratrace levels of uranium by selective laser excitation of precipitates" by Johnston and Wright (1981)]. In this work, selective excitation of probe ion luminescence is applied to the analysis of uranium co-precipitation in to calcium fluoride; and also "Detection of Ultratrace Levels of Uranium In Aqueous Samples by Laser-Induced Fluorescence Spectrometry" (Perry et al., 1981)

3. On page 353 MATERIALS AND METHODS section of the manuscript as stated, "fission track registration technique was used for the assessment of uranium concentration level". In the fission track method, the small volume of water used might result in observation of small fluctuations in concentrations, caused by temperature differences or chemical gradients hence the result is not representative of the average value in surface water or ground water. Laser-induced fluorescence is a direct and reliable method for the measurement of low uranium concentrations when the number of samples is very large. However, of the direct methods, the fission track method seems to be the nearest competitor.

4. Experimental data for the relationship of standard uranium concentration (c) and T and 'spiked' samples should be given. This method requires constant checking and recalibration. The reliability/quality of measurement results of water samples depend on strict adherence to each step of sampling, preservation of samples, time-interval between sampling and analysis (for filtered but unacidified water samples) and on the methodology adopted and not simply analysed by any person or laboratory or any technique.

I hereby request the authors to kindly further document the reliability of their findings as stated above.

REFERENCES

- American Public Health Association (APHA) (1980). Standard methods for the examination of water and waste water, 15th Ed. American Public Health Association. Washington DC.
- International Atomic Energy Agency (IAEA) (1973). Uranium exploration methods. Proceedings of a panel on uranium exploration methods held in Vienna, 10-14 April 1972.
- International Atomic Energy Agency (IAEA) (1988). Geochemical exploration for uranium. IAEA, Vienna. TRS No. 284.
- Johnston MV, Wright JC (1981). Determination of ultratrace levels of uranium by selective laser excitation of precipitates Anal. Chem. 53: 1050-1054.
- Perry DL, Klainer SM, Bowman HR, Milanovich FP, Hirschfeld T, Miller S (1981). Detection of ultratrace levels of uranium in aqueous samples by laser-induced fluorescence spectrometry. Anal. Chem. 53:1048-1050.
- Robbins JC (1978). Field techniques for the measurement of uranium in natural water. CIM Bull. 71:61-67.