

*Letter to Editor*

**Query related to publication titled “Geochemical modeling of uranium speciation in the subsurface aquatic environment of Punjab State in India” by Ajay Kumar, Sabyasachi Rout, Usha Narayanan, Manish K. Mishra, R. M. Tripathi, Jaspal Singh, Sanjeev Kumar and H. S. Kushwaha, Published in Journal of Geology and Mining Research Vol. 3(5), pp. 137-146, May 2011. Available online <http://www.academicjournals.org/jgmr> ISSN 2006 – 9766 ©2011 Academic Journals**

**Dr. D. P. S. RATHORE**

Accepted 7 May 2013

Incharge,  
Chemical Laboratory,  
Central Region,  
Atomic Minerals Directorate for Exploration and Research,  
Department of Atomic Energy,  
Civil Lines, Nagpur-440001(MS), India.

Dear Editor,

I have read the above cited paper very carefully. Undersigned has been involved in the analysis of geological materials and hydrogeochemical reconnaissance surveys attached with mobile geochemical laboratories in different parts of India for uranium exploration activities of Atomic Minerals Directorate for Exploration and Research. I have also contributed on uranium determination in diverse matrices vide my publications: D. P. S. Rathore, Manjeet Kumar and P. K. Tarafder, *Accred Qual Assur* 17 (2012)75–84; D. P. S. Rathore, *Talanta* 77 (2008)9–20; D. P. S. Rathore, *Explor Res At Miner*, 17 (2007)145-149; D. P. S. Rathore and Manjeet Kumar, *Talanta* 62 (2004) 343–349; P. K. Tarafder, L. Kunkal, P. Murugan and D. P. S. Rathore, *J. Radioanal. and Nucl. Chem.*, 253 (2002)135-142; D. P. S. Rathore, P. K. Tarafder, M. Kayal and Manjeet Kumar, *Analytica Chimica Acta* 434 (2001) 201–208; Manjeet Kumar, D. P. S. Rathore and Ajai K. Singh, *Mikrochim. Acta* 137 (2001)127-134; Manjeet Kumar, D. P. S. Rathore and Ajai K. Singh, *Fresenius J. Anal. Chem.*, 370 (2001) 377-383, Manjeet Kumar, D. P. S. Rathore and Ajai K. Singh, *Analyst*, 125 (2000) 1221–1226 and also my three recent publications: D.P.S. Rathore, *J. Radioanal. Nucl. Chem.*, DOI: 10.1007/s10967-013-2449-3, Published Online: 9 March 2013, DOI: 10.1007/s10967-013-2445-7, Published online: 24 February 2013 and DOI: 10.1007/s10967-013-2432-z, Published Online: 27 February 2013. 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) For un-acidified water samples, time interval between water collection and analysis. Water sample should be analysed on the same day.
  - (c) Methodology adopted for uranium analysis. A choice of an appropriate fluorescence enhancing reagent for different types of sample matrices is essential. Moreover, there are different methods of uranium analysis by laser-induced fluorimetry depending on the sample matrix.

Complete and unequivocal preservation of samples, whether domestic waste water, or natural water, is a practical impossibility. The physico-chemical 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 preferably on the same day (APHA, 1980; IAEA, 1973, 1988).

(2) On page, 139 of the manuscript quote "The above characteristics of water which are important for modeling of speciation are impossible to preserve in a collected sample and so must be measured in the field" unquote. At the same time stated in the section, Laboratory analysis: "The collected ground water samples were filtered through 0.45 micron filter paper, acidified with 0.01 M of nitric acid....."

Water samples should be filtered before collection or should be filtered on the same day and acidified with AR nitric acid to pH 1. What was the time-interval between collection of water samples and filtrations of collected ground water samples for acidification, for analysis of uranium, major cations and anions at the base laboratory (it is not clearly stated in the manuscript).

(3) As per my observations, this time-interval between collection of water samples and filtrations of collected ground water samples for acidification, for the analysis later at base laboratory is a critical and most essential parameter for ensuring reliability of measurement results. For accurate and reliable results, 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.

Some water samples were analysed for uranium, major cations and anions after varying time intervals. My observations were as follows:

- (i) There were more variations in uranium contents in water samples containing suspended or particulate materials. Variation in uranium values were up to the order of 50% and more depending upon the amount of suspended or particulate materials present. However, in some samples, the order of variations were very high, especially from areas in Rajasthan, India containing fluoride.
- (ii) Calcium values were found to be reduced by 6 to 60% in 15 to 20 days time-intervals but magnesium contents do not vary significantly in general, except in few samples.
- (iii.) Conductance, pH, carbonate, bicarbonate also change significantly.
- (iv) Nearly all water samples were found to contain suspended or particulate material.

### **Change in pH –alkalinity-carbon dioxide balance and calcium content**

pH may change significantly in a matter of minutes, dissolved gases may be lost (oxygen and carbon dioxide) with changes in pH- alkalinity-carbon dioxide balance, precipitation of calcium carbonate takes place (solubility product of  $\text{CaCO}_3 = 4.8 \times 10^{-9}$ ), thereby causing a decrease in the values for calcium and total calcium plus magnesium contents. Besides this, fluoride concentration which ranges from 1 to 60 ppm levels particularly in areas of Rajasthan, probably significantly reduces the calcium content through precipitation of calcium fluoride on storage. Calcium fluoride is insoluble and settles down (solubility product of calcium fluoride =  $4.0 \times 10^{-11}$ , magnesium fluoride =  $6.5 \times 10^{-9}$ ). The same is applicable for areas of Punjab, India.

A close examination of calcium and magnesium content in sets of samples (received from Dist. Barmer, Rajasthan and Haryana State) showed that some samples have less calcium content than that of magnesium. But, on comparing the results of samples with the usual trend of calcium to magnesium ratio, that is, average calcium and magnesium content of ground waters from different rock types (waters from granites – Ca-27 ppm; Mg-6.2 ppm; serpentinite, Ca-9.5 ppm; Mg-51 ppm; Shale Ca-227 ppm; Mg-29 ppm), it appears that the surrounding rocks are magnesium rich (may be ultramafic, etc) and should have comparatively less uranium, sodium and potassium contents. On the contrary, sodium

and potassium were also high and uranium concentrations were in the range of 14 to 49 µg/L.

On careful visual examination, whitish deposit/suspended material in sample bottles were noticed and verified experimentally by performing chemical analysis after acidification of sample with nitric acid. The acidified samples were analyzed for calcium and total calcium plus magnesium contents. Calcium contents were found significantly much higher in same samples in comparison to un-acidified analyzed samples, that is, calcium to magnesium ratio changes significantly. Calcium may also precipitate as calcium sulphate (solubility product of calcium sulphate =  $9.1 \times 10^{-6}$ ). The losses of calcium content through precipitation do not follow a uniform pattern. However, in some samples, an increase in calcium and magnesium values have been found, this increase is presume to occur when suspended particulate material with comparatively high calcium and magnesium levels slowly equilibrates with the water.

On page 139 and 140 of the manuscript, vide Table 1, as stated in the manuscript, quote "The high mean ratio(>1) of  $Mg^{++}/Ca^{++}$  in groundwater indicated.....". This is opposite of the usual trend of calcium to magnesium ratio, that is, average calcium and magnesium content of ground waters from different rock types (waters from granites – Ca-27 ppm; Mg-6.2 ppm; serpentinite, Ca-9.5 ppm; Mg-51 ppm; Shale Ca-227 ppm; Mg-29 ppm), it appears that the surrounding rocks are magnesium rich (may be ultramafic, etc) and should have comparatively less uranium, sodium and potassium contents. On the contrary, sodium and potassium were also high and uranium concentrations were in the range of 14 to 49 µg/L. With passage of time, there will be decrease in conductance, major cations and anions content. Sometime, magnesium content will be more than the calcium contents in these water samples, which is incorrect. In water samples, calcium contents, in general, is always more than magnesium (undersigned developed an indicator: D. P. S. Rathore, P. K. Bhargava, Manjeet Kumar and R. K. Talra, indicator for the titrimetric determination of calcium and total calcium plus magnesium with ethylenediaminetetraacetate in water, *Analytica Chimica Acta*, 281(1993) 173-177); D. P. S. Rathore, Manjeet Kumar and P. K. Bhargava, a study of indicator properties of the o-Hydroxyazo Dye, *Chem. Anal.*, 40 (1995) 805-813; D. P. S. Rathore, Manjeet Kumar and P. K. Bhargava, Complexometric determination of Calcium and Magnesium in Dolomite, Limestone, Magnesite, Phosphatic and Silicate Matrices using Azochromotropic acid derivative as an indicator, *Chem. Anal.*, 42 (1997) 725-728).

In my opinion and based on my observations as stated above, this conclusion is incorrect and highly misleading. This interpretation in the manuscript, based on the unreliable measurement results obtained (the high mean ratio (>1) of  $Mg^{++}/Ca^{++}$  in groundwater), is simply due to variations in the contents of calcium and magnesium contents with time-interval between collection of water samples and filtrations of collected ground water samples for acidification, for analysis of uranium, major cations and anions at base laboratory and need to be further validated.

### Changes in Uranium contents of water samples

Uranium levels also changes considerably probably due to adsorption, co-precipitation etc. In presence of fluoride, fine suspension or precipitation of uranium fluoride may take place, which is a well known co-precipitation of uranium. This, may result in abnormal variations in uranium levels, if, samples are not properly acidified and stored. High acidity is essential to keep uranium in solution in presence of fluoride. The abnormal behavior of fluoride needs further investigation. It is necessary that before acidification of water sample, it should be 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 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.

On page, 139 of the manuscript, stated in the section, Laboratory analysis: "the collected ground water samples were filtered through 0.45 micron filter paper, acidified with 0.01 M of nitric acid....." It is very clearly stated that the samples were filtered through 0.45 µm Millipore membrane filter before taking up for analysis. The water samples were not filtered and acidified prior to collection for storage in clean polythene containers. What is the reliability of such samples for further analysis, if un-acidified samples have not been analysed on the spot or not properly acidified for storage for analysis later at base laboratory? What was the time interval between collection of water samples and analysis performed (not stated in the manuscript).

High total dissolved salts (TDS) in water samples results in larger variation in major cations and anions, uranium contents with respect to time-interval between collection and analysis. This variation in these contents depends on TDS. 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 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 water sample in the container (probably calcium fluoride,  $CaF_2$ ), as it is a very good co-precipitant of uranium, it adsorbs uranium from the whole sample volume. So, 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 ppm has been reported in this part of 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 M. V. Johnston and J. C. Wright, *Anal. Chem.*, 53(1981) 1050-1054. 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", by D. L. Perry, S. M. Klainer, H. R. Bowman, F. P. Milanovich, T. Hirschfeld, S. Miller, *Anal. Chem.* 53 (1981) 1048-1950).

On page 139 of the manuscript, in the experimental section, Uranium: As stated in the manuscript "The concentration of uranium in groundwater was measured by a laser fluorimeter (Quantalase Laser Fluorimeter, Indore, India) in which a pulsed nitrogen laser is used to excite uranyl species at 337.1 nm. 5% Phosphoric acid in ultra pure water was used as fluorescence reagent." In laser fluorimetry, the choice of the fluorescence-enhancing reagent is of great importance and depends mainly on the matrix composition (presence of quenching and/or absorbing species) and uranium concentration level. For water samples, the best fluorescence enhancing reagent is 5% sodium pyrophosphate solution in distilled water adjusted to pH 7.0 to 7.2 by drop-wise addition of orthophosphoric acid (as per the manual of the instrument). With phosphoric acid as fluorescence enhancing reagent, the sensitivity of the Quantalase Laser Fluorimeter instrument will be further decreased. Moreover, there will be severe quenching of uranyl fluorescence by chloride ion. It is practically impossible to measure uranium concentration levels of 1 to 2 ppb in water samples using the calibration suggested by the authors. In addition to, highly saline water samples require sample preparation for the removal of chloride (strong quencher) followed by measurement using laser fluorimetry. These high values on uranium contents in water samples needs to be validated by conventional pellet-fluorimetry technique. Moreover, this miniaturized version of the instrument lacks in consistencies in the signal response (low performance qualification, PQ) for its varied utility for the determination of uranium in the aqueous solutions of diverse matrices on routine basis as well as for control laboratory (D. P. S. Rathore, *Talanta* 77 (2008)9–20). What is the reliability of uranium determination as stated above using 5% phosphoric acid in ultra pure water as fluorescence reagent?.

Authors are advised to go through the manual of UA-3 uranium analyser, also the manual of the instrument and publications: D. P. S. Rathore, P. K. Tarafder, M. Kayal and Manjeet Kumar, 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(2001) 201–208; D. P. S. Rathore, Advances in Technologies for the Measurement of Uranium in Diverse Matrices (Review article), *Talanta* 77(2008) 9–20; J. C. Robbins, "Field techniques for the measurement of uranium in natural water", *C. I. M. Bull.*, 71 (1978) 61–67and the references therein; J. C. Robbins, J. D. Kinrade, United States Patent, patent no.4,239,964 (December 16, 1980); J. C. Robbins, C. Castledine, W. Kostiak, Analytical Procedures for UA-3 Uranium Analysis—Applications Manual, Scintrex Limited, Ontario, Canada, 1985 Oct.).

## SUGGESTIONS

Hydro-geochemical reconnaissance survey programme for geochemical modeling of uranium speciation in the subsurface aquatic environment seems to be very simple in terms of sampling, analytical techniques, interpretation of data etc., but in fact, it is a difficult and most challenging task. It is due to the fact that the degree of variations in the contents of major cations and anions, and uranium contents are in a un-predictably significant manner as stated above, if the elapsed time-interval between sampling and analysis is more for unfiltered and unacidified water samples, leading to erroneous results and their interpretations. The sample must not be contaminated with the elements to be determined and should not undergo physicochemical 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 following are the steps for the self-evaluation of data of water samples:

1. pH, conductance and temperature etc. should be measured at site of sample collection.
2. The exploration scientist's first critical scrutiny should be directed at the entire sample collection process to guarantee a representative sample for analysis and to avoid any possible losses of contamination during collection.
3. Attention should also be given to the types of container and to the manner of transport and storage. Water samples should be collected in polyethylene bottles, using a rapid sampling system after filtration of sample under pressure.
4. A periodic re-assessment should be made of methods with respect to the sensitivity precision and accuracy of sample collection and its analysis. Intra-laboratory as well as inter-laboratory evaluations should be carried out.
5. Control samples should be prepared. Control samples can be natural water samples or samples with standard

additions (natural water with one or more chemicals added e.g. tap water that have been assayed by several “referee” laboratories preferably by several different methods providing good agreement, so that a “known” value can be assigned to the sample. Synthetic control samples can also be prepared to assess the accuracy of results. Control charts prepared from the data obtained by re-cycling about 20% of the samples (duplicate samples) for duplicate determinations along with each of set of samples, can be used to check the precision of the determination (“Standard methods for the examination of water and waste water” 15<sup>th</sup> Ed.1980, “American Public Health Association, Washington).

6. The expression of analytical results in milligram-equivalents permits one to check, to a certain degree, the accuracy of analysis performed, since in this case, the sum of milligram equivalents of the cations must obviously equal the sum of the milligram equivalents of the anions. This relation will hold good, when analysis is performed promptly within 2 to 3 days, then the error will be within 2 to 3% limit, which is an indication of satisfactory analysis.

7. The analytical data of hydro-geochemical samples should be tabulated in the form of maps for future developments. Following points will be more useful:

- i) Time interval of collection of sample and analysis undertaken should be mentioned.
- ii) Exact sample location along with the rock types of areas should be mentioned.
- iii) The level of seasonal variations, if any, should also be recorded.
- iv) Analytical data of samples should be reflected in maps along with other analytical data obtained by other geochemical surveys.
- v) The methods adopted for chemical analysis of samples should be reflected in the final report.

These above points / suggestions will be highly useful to uncover weaknesses in the analytical chain and permit improvement to be instituted without delay. The results can disclose whether the trouble stems from faulty sample collection / treatment, poor calibration practices, impure or incorrectly standardized reagents.

In general, shorter the time that elapses between collection of a sample and its analysis; the more reliable will be the analytical results. Water samples should be collected and stored in polyethylene bottles after filtration of samples under pressure to avoid contamination from suspended or particulate materials. Hydro-geochemical surveys for exploration of uranium warrant the need and use of “Mobile Geochemical Laboratory”. It is recommended that the analysis should be performed on the same day of sample collection, depending upon the nature of determination. In addition to this, self-evaluation of data in the light of above points is highly desirable for providing quick feedback of analytical data to understand and interpret the true nature of water samples for geochemical interpretation.

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 lab 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. 53:1048-1950.
- Rathore DPS (2008). Advances in Technologies for the Measurement of Uranium in Diverse Matrices (Review article). Talanta 77:9-20.
- 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.
- 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.
- 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
- Rathore DPS, Bhargava PK, Kumar M and Talra RK (1993). Indicator for the titrimetric determination of calcium and total calcium plus magnesium with ethylenediaminetetraacetate in water, Anal. Chim. Acta, 281:173-177
- Rathore DPS, Kumar M, Bhargava PK (1995). A study of Indicator Properties of the o-Hydroxyazo Dye, Chem. Anal., 40:805-813
- Rathore DPS, Kumar M, Bhargava PK (1997). Complexometric determination of calcium and Magnesium in Dolomite, Limestone, Magnesite, Phosphatic and Silicate Matrices using Azochromotropic acid derivative as an indicator, Chem. Anal. 42:725-728.
- Rathore DPS, Tarafer 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.

Robbins J C, Castledine C, Kostiak W, *Analytical Procedures for UA-3 Uranium Analysis—Applications Manual*, Scintrex Limited, Ontario, Canada, 1985.

Robbins JC (1978). Field techniques for the measurement of uranium in natural water, *C. I. M. Bull.*, 71 61–67 and the references therein.

Robbins JC, Kinrade JD (1980). United States Patent, patent no.4, 239, 964 (December 16, 1980).