

## Heavy Toxic Elements Distribution in the Drinking Water Samples

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### Abstract

Uranium and other heavy toxic elements distribution in the drinking water samples of SW-Punjab, India, are presented. It is mandatory in all publications to clearly mention the instrumental details to ensure reliability of measurement results. The same fluorescence enhancing reagent should be used for calibration of the instrument and subsequent measurement of uranium in samples. Using the above procedure for pre-concentration and keeping in view of the characteristic concentration of these heavy metals using flame Atomic Absorption Spectrophotometer, their determination at  $\mu\text{g l}^{-1}$  concentration levels is practically impossible. Interpretation and conclusions based on such unreliable results on uranium and other heavy metals will be highly misleading for their health risk, toxicological risk and chemical toxicity risk assessments.

**Keywords:** Radionuclide; Uranium; Radiological risk; Toxicity; Laser fluorimetry

### Comments

I have read the paper 1 and all the cited references in this manuscript. I would like to share some of my observations on this manuscript which may be useful for future research and a meaningful publication.

In Experimental techniques, it is stated that Laser fluorimeter manufactured by Quantalase Enterprises Pvt. Ltd., Indore, India was used for analyses of water samples for uranium concentrations in this work. The Quantalase Enterprises Pvt. Ltd., Indore, India/RRCAT, Indore, India has manufactured a number of fluorimetry instrument models differing in specifications as well as in performance qualifications [1-3]. It is mandatory in all publications to clearly mention the instrumental details and methods of measurement including all the steps of sampling and preservation, etc., to ensure reliability of measurement results [3-15]. The model number of the instrument is missing in cited publication1.

Analytic procedure, as stated, quote "Analytic procedure begins with taking 10 ml aliquot of filtered water sample in duplicate for wet digestion ( $\text{HClO}_4$  and  $\text{HNO}_3$ ) on hot plates to destroy organic material in the sample" unquote. Moreover, authors further stated that quote "The residue was then dissolved in Millipore elix-3 water followed by mixing with fluorescence reagent (5% sodium pyrophosphate) to make the total volume 25 ml and to adjust pH to 7.2 levels. The sample solution was then taken into a cuvette for the measurement of U concentration" unquote. On the other hand, authors further stated that quote "The instrument was calibrated in the range of 1-100  $\mu\text{g l}^{-1}$  using a stock solution of standard that was prepared by dissolving 1.78 g of uranyl acetate dihydrate ( $\text{CH}_3\text{COO})_2\text{UO}_2 \cdot 2\text{H}_2\text{O}$ ) in 1 liter of Millipore elix-3 water containing 1 ml of  $\text{HNO}_3$  (70% pure). 5% phosphoric acid in ultra-pure water was used as fluorescence reagent. To obtain blank counts, a blank sample containing same amount of fluorescing reagent was measured for U concentration" unquote. The same fluorescence enhancing reagent should be used for calibration of the instrument and

subsequent measurement of uranium in samples. The procedure adopted for uranium determination is wrong. Further statement and claim by the authors quote "Quality assurance was made by analysis of IAEA standard reference materials, spike recovery, replicate analysis, and cross method checking" appears highly misleading.

Laser-induced fluorescence is very sensitive, selective and fast method for ultra-trace uranium determination especially needed for hydrogeochemical reconnaissance surveys [2,4-7]. Any additional chemical preparation of sample will introduce contamination and high blank value [6-8]. A choice of an appropriate fluorescence enhancing reagent for different types of sample matrices is essential for the reliable determination of uranium using laser fluorimetry [2,4,7]. Moreover, there are different procedures reported for different type of sample matrix followed by laser-induced fluorimetry [2,5,8]. Truly, the reliability of analytical results depends on strict adherence to the various steps of the validated method and not on fluorimetry technique or laboratory or a person [3-15]. Direct methods for the analysis of uranium in natural water samples should be adopted. For water samples, the best fluorescence enhancing reagent is 5% sodium pyrophosphate solution in distilled water adjusted to pH 7.0-7.2 by drop-wise addition of orthophosphoric acid (as per the manual of the instrument). Highly saline water samples require sample preparation [7], the high uranium content in such samples needs to be validated by conventional fluorimetry technique and level of variation, if any, have been documented. Authors are advised to go through the application manual of UA-3 uranium analyser, also the manual of the instrument and other publications. The presence of fluoride may significantly affect the changes in uranium content [9-15].

Elemental analysis in water using atomic absorption spectrophotometry and analytic procedure, in the manuscript 1, as stated by authors, quote "100 ml aliquot of filtered water sample was taken in duplicate for wet digestion ( $\text{HNO}_3$ ) on hot plates to destroy organic material in the sample. 25 ml of the prepared sample was injected in the nebulizer-spray chamber-burner system of the Atomic Absorption Spectrophotometer. Air-acetylene compressed gas has been used as oxidant and fuel. Atomic Absorption Spectrophotometer was standardized with standard element concentrations in prior" unquote

and as claimed by authors in the manuscript regarding heavy metal concentration (The heavy metal concentration variations observed in drinking water samples of the study region is reported). The manufacturer and model number of the instrument is missing [1]. Using the above procedure for pre-concentration and keeping in view of the characteristic concentration of these heavy metals [16] (characteristic concentration [mgL<sup>-1</sup>/1% Abs]: for As, 0.68 at 193.7 nm; Pb-0.3 at 283.3 nm; Cu-0.035 at 324.8 nm; Mn-0.03 at 279.5 nm; Co-0.075 at 240.7 nm; Ni-0.07 at 232.0 nm; Fe-0.08 at 248.3 nm; Zn-0.012 at 213.9 nm and Cr-0.05 at 357.9 nm) using flame Atomic Absorption Spectrophotometer, their determination at 4 µg<sup>-1</sup> concentration levels is practically impossible. This claim by the authors is absolutely incorrect and highly misleading” I (strongly) disagree with their statement in the manuscript.

The use of instrumental methods [16-20] for trace metal ion determinations frequently requires pre-concentration procedures. Methods widely used for pre-concentration are based on liquid-liquid extraction, ion exchange and chelating resins [18-20]. The chelating resins [18-20] are capable of preconcentrating metal ions selectively from a large volume and may be easily coupled with flame atomic absorption spectrometry (FAAS) to enhance its sensitivity.

The manuscript, quote that “the authors are extremely grateful and sincerely acknowledge the guidance, help in sampling, encouragement and consistent involvement of Dr. R.M. Tripathi and Dr. S.K. Sahoo, BARC, Mumbai during this work” unquote. The authors are acknowledging themselves (R.M. Tripathi and S.K. Sahoo).

## Conclusion

Interpretation and conclusions based on such unreliable results on uranium and other heavy metals will be highly misleading for their health risk, toxicological risk and chemical toxicity risk assessments.

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