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Improved method for the complete separation of gross alpha and beta in drinking water

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ABSTRACT

During this work, a modified methodology for the separation of gross alpha and beta activity from potable water was established. Complete separation of gross alpha activity was carried out by $Fe(OH)_3$ and $BaSO_4$ precipitation whereas gross beta activity was scavenged by Ca-oxalate and AMP (ammonium molybdate phosphates). The validation of the results was carried out by laboratory spiked experiments, which show a recovery of gross radioactivity in the range of 90–98% with the new methodology. The detection limits using this methodology are 20 mBq/l and 2 mBq/l for gross beta and alpha respectively. These detection limits are two orders of magnitude lower than the maximum acceptable concentration as prescribed by World Health Organisation (WHO) of gross alpha and gross beta activity i.e. less than 0.1 Bq/L and 1 Bq/L, respectively.

Keywords: Potable water; Gross alpha and beta radioactivity; Separation; Drinking water limits; Uranium; Cs-137

1. Introduction

Important primordial nuclides in nature are the long-lived nuclides thorium-232 (Th-232), uranium-235 (U-235) and uranium-238 (U-238) as well as potassium-40 (K-40). Thorium and uranium are concentrated in crustal rocks in an average Th:U ratio of about 3.5. However, various igneous, metamorphic and sedimentary rock types have widely different U and Th concentrations. Some metamorphic rocks, for example, have a high abundance of U and Th. U is also found to be strongly enriched in certain organic sediments, e.g. peat, lignite and asphalt. In a closed system the progeny of Th and U are present in concentrations determined by the concentration of parent U and Th isotopes and the time since the system became closed to nuclide migration. In nature, closed systems rarely exist and predictions regarding nuclide concentrations in water bodies invariably include large uncertainties. These nuclides and their decay products are found in ground and spring waters in element specific concentrations dependent on complex hydrogeologic processes and conditions (dissolution, transport and ion-exchange processes as well as redox potentials and pH-conditions of the aqueous system). These hydrogeologic processes result in non-equilibrium conditions between parent nuclides and their progeny [1,2]. These radionuclides account for almost the entire radioactivity present in drinking-water. Traces of radioactive fallout from above ground nuclear weapons tests are detectable in the environment but their contribution to drinking-water radioactivity is negligible. The magnitude of the dose from ingesting water is to a large extent determined by those nuclides that have high dose coefficients and remain in solution.

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In setting dose guidelines for radionuclides in drinking water, it is recognized that water consumption contributes only a portion of the total radiation dose and that some radionuclides present are natural in origin and therefore cannot be excluded. Consequently, maximum acceptable concentrations for radionuclides in drinking water have been derived based on a committed effective dose of 0.1 mSv from one year's consumption of drinking water. This dose represents less than 5% of the average annual dose attributable to natural background radiation. Hence water samples should be initially screened as per WHO guidelines shown in Fig. 1 for radioactivity using techniques for gross alpha and gross beta activity determinations [3]. Compliance with the guidelines may be inferred if the measurements for gross alpha and gross beta activity are less than 0.1 Bq/L and 1 Bq/L, respectively, as these are lower than the strictest maximum allowable concentrations (MACs). Simulated laboratory experiments clearly show that presently used methodology for the estimation of gross alpha and beta in drinking water is inefficient. As per these methods, all the alpha and beta emitting radionuclides do not efficiently scavenge. During this work, a selective and more efficient methodology is proposed for the separation of gross alpha and gross beta in drinking water.

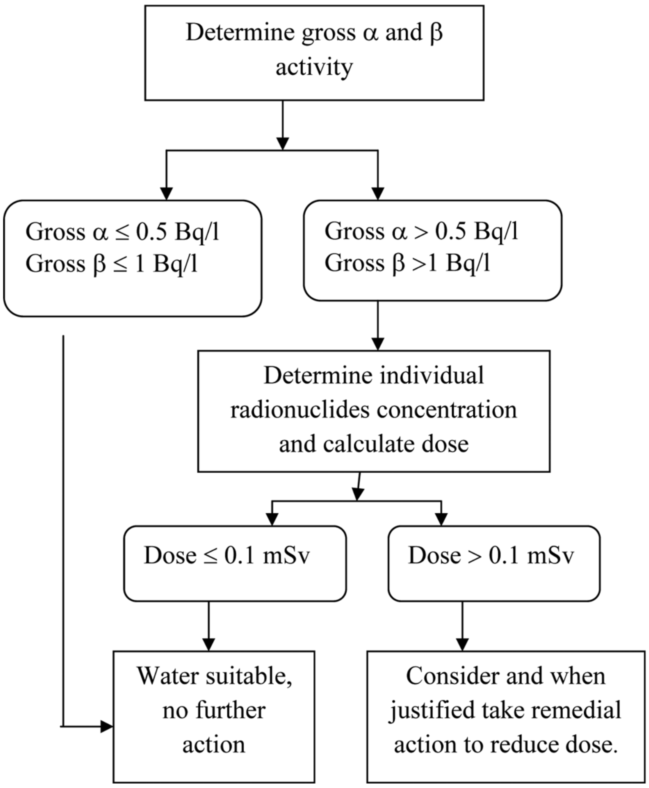

Fig. 1. Application of World Health Organisation guidelines for radionuclides in drinking water.

2. Material and method

2.1. Sample collection

Two types of samples were used for this work. Type 1 sample consists of six different brands of commercially available mineral drinking water bottles collected from different parts of Mumbai, India. Type 2 set of samples was collected from four different wells around Trombay, Mumbai having latitude 19°00′498 (N) and longitude 72°55′136. In the case of commercial mineral water sample, a standard set of 1 L was brought to the laboratory. Each sample was collected in triplicates. In the case of well water, 5 L of samples were collected in pre-cleaned polypropylene canes. After filtration through 0.45 μm filter paper, two aliquots of 1 L each were taken and analysed for gross alpha and beta activity separately. Other aliquots were spiked with standard solutions of $U_{natural}$ and Ra-226 for gross alpha and Cs-137 in the case of beta. A small quantity of acid was added as a preservative.

2.2. Measurement of major anions and cations

Concentrations of various anions and cations in the sample were measured using an ion exchange chromatography system Dionex-600. Calibration of the instrument was done using a mixed anion and cation standard source from Dionex.

2.3. Methodology for the separation of gross alpha and beta

A flow diagram for the separation of gross α and β by general methodology is shown in Figs. 2 and 3 respec-

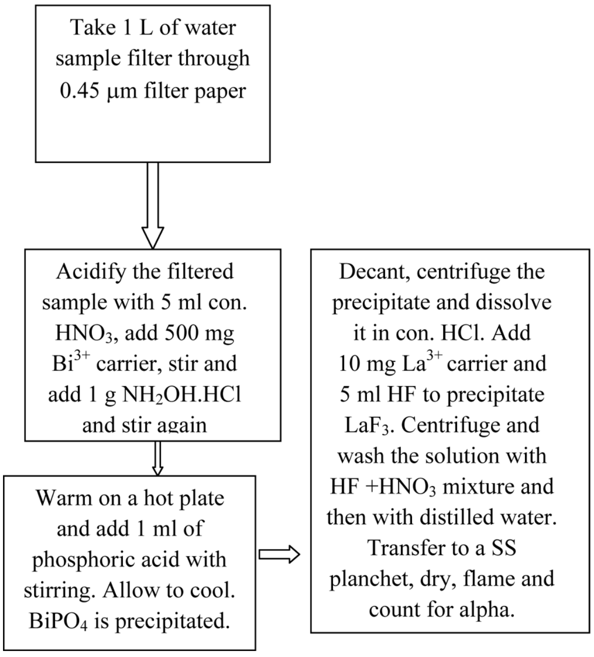

Fig.2. Flowchart for general method used for separation of gross alpha activity.

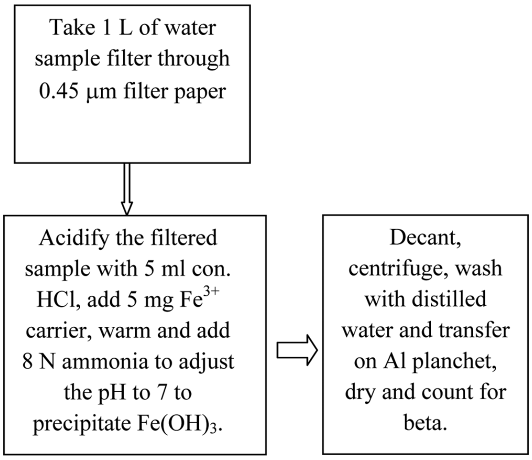

Fig. 3. Flowchart for general method used for separation of gross beta activity.

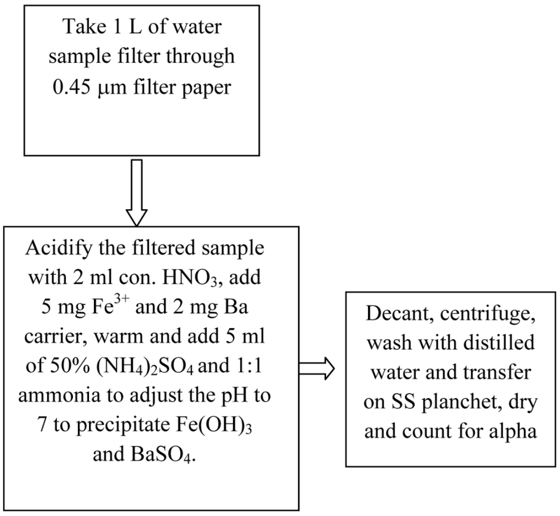

Fig. 4. Flowchart for modified procedure established for separation of gross alpha activity from aquatic medium.

tively whereas their modified procedure is given in Figs. 4 and 5 respectively.

2.4. Measurement of gross alpha activity

The measurement of gross alpha was carried out using ZnS(Ag) detector having a background of 0.07 cpm and counting efficiency of 39%. The efficiency of the system was evaluated using Am-241 having an activity of 83.33 Bq. This electrodeposited source was prepared using standard solution of Am-241 received from IAEA. This electrodeposited source was calibrated against a mixed nuclide source of Am-241 from Amersham (AMR 33).

2.5. Measurement of gross beta activity

Gross beta counting was carried out using a gas flow counter, in which two planar GM counters are mechanically arranged in such a way that background radiation due to cosmic rays and surrounding materials does not interact directly with the medium of the main counter where the sample is placed without passing through the guard counters. The counters have an aluminium or gold foil window of about 1.0 mg/cm^2 through which the β particles traverse and reach the gas (argon) chamber with isopropyl alcohol vapours and ionise the medium. The signals from both counters are collected through the anode wire. The electronic signals from both main and guard counters are fed to an anticoincidence electronic unit. The unit filters out the signal of the main counter if it has a corresponding signal of the guard output in coincidence within a specified resolving time. Due to anticoincidence technique and shielding, the background of the system is reduced to about 0.8–1.0 cpm. The efficiency

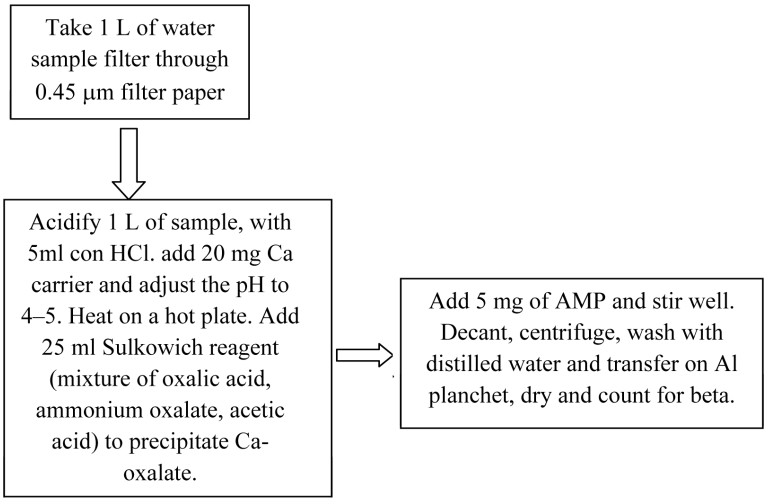

Fig. 5. Flowchart for the modified procedure established for separation of gross beta activity from aquatic medium.

of the system for K-40 is 31% and is measured using a source with an activity of 3.33 Bq. A standard source for beta was prepared in-house using salt of KCl with natural abundance (0.012%) of K-40.

3. Results and discussion

Selective separation of gross alpha and beta emitting radionuclides at trace levels from the potable water taken from different geological matrices is involved, complex radiochemical separation techniques. The concentration of these radionuclides in terms of mass is of the order of 10^{-12} g l^{-1} At such a low level it is difficult to work with separation chemistry without the help of carriers (stable counter parts for different radioelements). To avoid the effect of self-attenuation carrier during the course of measurement, only an optimum quantity is recommended. As a thumb rule, the prescribed surface density should not be more than 10 mg cm^{-2} and 50 mg cm^{-2} in the case of gross alpha and beta respectively. In view of this, there is a limitation on the amount of stable carriers to be used in radiochemical separation of gross alpha and beta radioactivity.

Tables 1 and 2 give the various physiochemical characteristics of the bottled mineral drinking water and well water samples taken for the analysis. Although there is large variation in the mineral composition of the bottled water and ground water samples taken for the analysis, in both cases there is no interfering major cations like NH_4^+ which interfere in the separation of Cs^+ and anions like HCO_3^-, which enhances the solubility of Ra. Because of higher concentration of HCO_3^- in freshwaters, around limestone regions radium is found in the highest concentration. Ra-228 is also found in excess of its parent Th-232 in natural waters in such region having dominance of HCO_3^- [4].

The dominance of radioactivity in the drinking water is mainly due to natural radionuclide like uranium, thorium and their progeny, K-40 and anthropogenic radionuclide like Cs-137 due to global fallout. The relative concentration of the ions of the primordial nuclides in water is stated to be in the order $U^{6+} > U^{4+} >> Th^{4+}$ [5,6]. Thorium is highly particle as it is reflected from its K_d value which is in the range of 10^6 [7]. As a consequence of this, ultra low level concentration of Th, as dissolved species and so on with its daughter products. In view of this daughter product of Th like Ra-228 can be neglected in drinking water. Whereas due to dissolved nature of uranium in aquatic medium its daughter product like Ra-226 cannot be ignored as constituents of aqueous systems. General methodology adopted for the separation of gross alpha and beta is shown schematically in Figs. 2 and 3. However both of these methodologies have certain disadvantages. In the case of alpha, separation of uranium was ineffective with $BiPO_4$ precipitation. In order to improve this, a modified procedure was adopted for complete separation of alpha, i.e. along with uranium (Fig. 4). The modified procedure for the estimation of gross alpha accounts for all alpha emitting actinides and Ra-alpha which is co-precipitated with $BaSO_4$. In this modified methodology, detection limits are further improved because there is no use of La which contributes to background alpha activity due to the presence of traces of U, which is an integral part of lanthanum chloride salt used for the preparation of La carrier solution. In order to validate the above mentioned fact, i.e. $BiPO_4$ does not carry efficiently U_{nat}, experiments were conducted with artificially contaminated drinking bottled waterwith uranium in the concentration range of 50–500 ng mL^{-1}. Results shown in Fig. 6 clearly indicate the recovery of uranium about 30–35% in the case of $BiPO_4$, whereas it is 90–95% in the case of modified method. Fig. 7 shows the recovery of gross alpha with $BiPO_4$ and Fe as $Fe(OH)_3$

Table 1
Physico-chemical characteristics of the sampled drinking water samples

Parameters	Range
pH	7.1–7.3
Total dissolved solids (TDS), ppm	150–170
Hardness, ppm	60–70
Bicarbonate, ppm	55–65

Table 2
Mean value of various physico-chemical characteristics of ground water before and after spiking

Sample (ID)	GW–1	GW–2	GW-3	GW-4
pH	7.8±0.2	7.9±0.1	7.7±0.1	7.9±0.1
E.C.μS	310±10	370±13	350±10	360±15
HCO_3^-, mg L^{-1}	190±15	220±15	223±18	230±15
F^{-1}, mg L^{-1}	0.08±0.01	0.07±0.01	0.03±0.01	0.08±0.01
Cl^{-1}, mg L^{-1}	19.01±1.61	17.3±1.21	20.0±1.3	23.0±1.3
PO_4^{3-}, mg L^{-1}	0.31±0.02	0.41±0.07	0.44±0.18	0.34±0.12
Na^+, mg L^{-1}	25.0±1.2	22.5±1.1	28.41±1.60	26.16±1.54

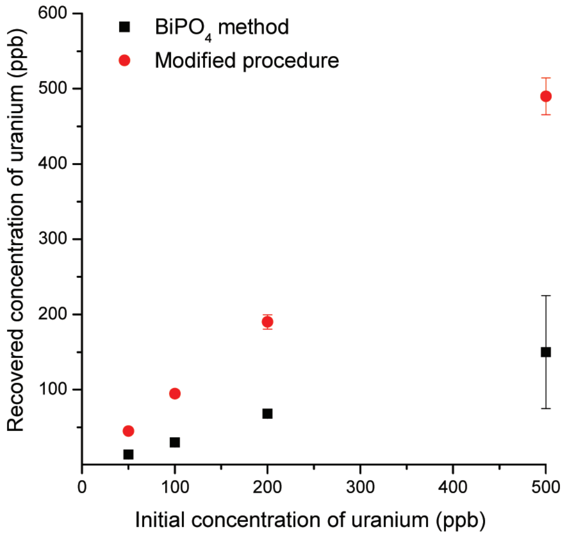

Fig. 6. Recovery of uranium by $BiPO_4$ and modified procedure at different concentration of uranium (contaminated with standard solution of uranium) in bottled water.

from spiked bottled mineral water and ground water with a standard solution of alpha. Results show that only 15% (groundwater)–30% (bottled drinking water) of the total spiked alpha was recovered by $BiPO_4$ precipitation, whereas 90–95% was recovered in the case of $Fe(OH)_3$ precipitation. Percentage recovery in the case of spiked samples was calculated after subtracting the background, i.e. the value of the blank sample. From this figure it is clear that with the new methodology the recovery for alpha emitting radionuclides was increased from 30% to 95% in the case of mineral water, whereas in the case of ground water it increased from 13% to 91%. The difference in the recovery of gross alpha activity in mineral and ground water is attributed to the complex matrix of ground water (various anions, cations, dissolved organic carbon, etc) which make the methodology slightly less effective in the case of ground water, however this needs further investigation.

As per the general methodology, effective separation of gross beta emitting radionuclides from water sample was carried out by precipitation of $Fe(OH)_3$, after addition of Fe carrier in the sample (Fig. 3). This process is not very effective for scavenging divalent elements like Ra and Sr and monovalent Cs and K [8]. Fig. 8 shows the recovery of Cs-137 and Ra-226 (although it is alpha emitting radionuclide but used as a chemical analogue of Ra-228) for the laboratory simulated experiment for ground water and bottled mineral water by using the general method. From this figure it is clear that the recovery for this element is only in the range of 38–50%. Therefore a modified methodology as shown in Fig. 8 was adopted for the complete beta separation from the water samples. As per this methodology, adjust the pH to 4–5 and Ca^{2+} as carrier and 25 ml Sulkowich reagent to precipitate Ca-oxalate and thereafter add a pinch of ammonium molybdate phosphates (AMP), which is a very selective binder for the Cs-137 at pH 1 [9]. Since the solution after addition of Ca^{2+} carrier and Sulkowich reagent have pH 4.5, therefore the experiment was conducted to see the recovery of Cs-137 at pH 4.5. Fig. 9 shows the recovery of Cs-137 from aquatic medium in the pH range of 1–7.

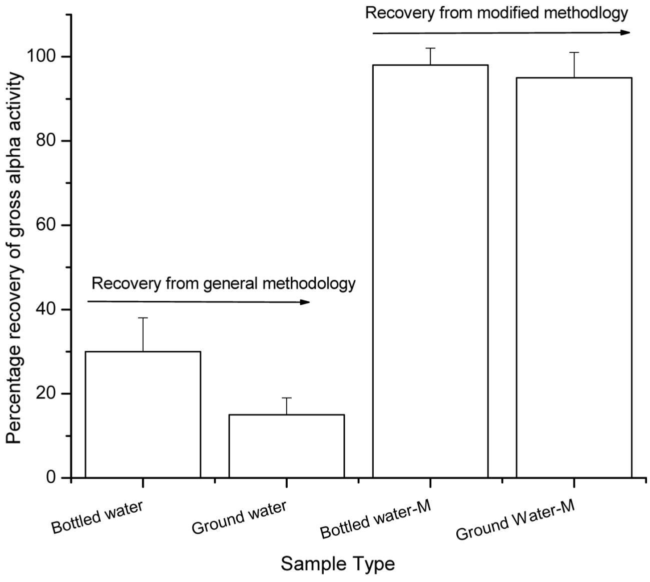

Fig. 7. Recovery of gross alpha activity from bottled mineral water and ground water by general and proposed modified methodology.

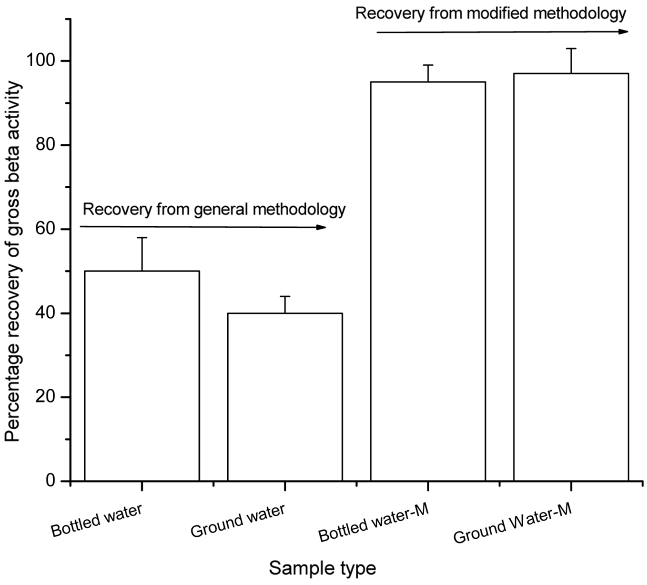

Fig. 8. Recovery of gross beta activity from from bottled mineral water and ground water by general and proposed modified methodology.

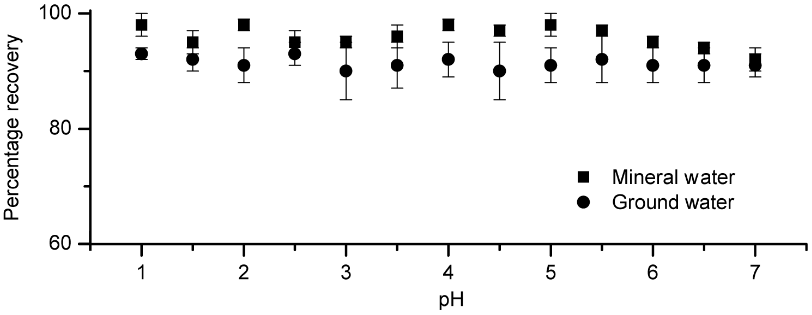

Fig. 9. Recovery of Cs-137 at different pHs from bottled mineral water and ground water.

From this figure, it is clear that the selectivity of Cs-137 remains the same at pH 4.5 as in the case of pH 1. The percentage recovery evaluated in the case of the spiked experiment with the modified procedure shows a recovery in the range of 93% and 98% in the case of mineral and ground water, respectively.

4. Conclusion

The process of identifying individual radioactive species and determining their concentration requires sophisticated and expensive analysis, which is normally not justified because the concentrations of radionuclides in most circumstances are very low. Therefore, a more practical approach was adopted for screening procedure, where the total radioactivity present in the form of alpha and beta radiation is determined, without regard to the identity of specific radionuclides. Criteria that are generally used for drinking water quality assessments can be expressed as a qualitative health risk, e.g. stated as increased morbidity or cancer risk. A quantitative health risk for exposure to radioactivity can be estimated by using a nominal value of 5% per Sievert. This value is for mortality from cancer after exposure to low doses for a population of all ages and as recommended by the ICRP [10]. Inclusion in the water quality guideline of a quantitative risk criterion expressed as a statistical mortality risk is, however, not recommended.

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