FAST DETERMINATION OF URANIUM AND RADIUM IN WATERS OF VARIABLE COMPOSITION

M. Ayranov^{1, 2*)}, U. Krähenbühl¹ and U. Schneider¹

¹ Department for Chemistry and Biochemistry, University of Bern, Freiestrasse 3, CH-3012, Bern, Switzerland

² Present address: European Commission, Joint Research Centre, Institute for Transuranium Elements, Hermann-von-Helmholtz-Platz 1 D-76344 Eggenstein-Leopoldshafen, Germany

The effects of uranium and its progeny radium are known to be harmful and their measurements in drinking water are necessary for careful monitoring. Fast and accurate methods for determination of uranium and radium in water samples with various salinity and activities concentrations have been developed. High Resolution Inductively Coupled Plasma Mass Spectrometry is used for direct measurement of uranium. Calibration is performed with ²³⁸U standards and ²⁰⁹Bi is used as internal standard to correct the matrix effects and plasma instability. The radium is determined by photon electron rejected alpha liquid spectrometry after a chemical separation procedure that includes co-precipitation of radium with barium sulphate, transformation of the sulphate to carbonate and extraction of radium in the scintillation cocktail. The minimal detectable activities of 3.5×10^{-8} Bq kg⁻¹ for uranium and 2.3×10^{-4} Bq kg⁻¹ for radium are obtained.

1 Introduction

Uranium appears in the earth's crust in an average concentration of 4 ppm [1]. ²²⁶Ra is a progeny of ²³⁸U decay and is considered one of the most toxic radioisotopes because of its high specific activity [2] and a metabolic behaviour similar to that of calcium.

Uranium and radium isotopes occur in fresh surface and drinking water from the rocks and soil with which water comes into a contact. The consumption of such water can cause a significant increase in the internal radiation dose to the population. In 1996 the World Health Organization (WHO) recommended that the gross α - and β - activities for drinking water should not exceed 0.1 and 1 Bq L⁻¹, respectively [3]. Therefore, the activity of each radionuclide in water has to be determined in order to evaluate the reference effective dose established by WHO - 0.1 mSv y⁻¹ [4]. These recommendations enforce a regular monitoring of the uranium and radium in surface waters, as well as the development of faster, more reliable and sensitive analytical methods [5].

The concentration of uranium and its progeny products in water are influenced by the chemical and physical characteristics of the aquifer, uranium content in the geological formation involved and its oxidation states [6]. The hexavalent uranium compounds are easily soluble in water, while tetravalent ones are less soluble [7, 8]. When rocks are exposed to weathering and water circulation a separation of uranium isotopes occurs, the ^{234/238}U isotopic ratios in the water are greater than 1, and the equilibrium between uranium and its progeny is altered [9].

^{*)}e-mail: marin.ayranov@ec.europa.eu

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The water quality for consumption has to be controlled in order to guarantee the mandatory low-level radioactivity. Many authors are using proven analytical methods for determination of low activities of uranium and radium isotopes: neutron activation analysis [10–12] alpha spectrometry [13–15], liquid scintillation [5, 15–18], and mass spectrometry [19–21]. Determination of 226 Ra requires an elaborate and time consuming sample preparation, especially at low concentrations. McDowell has proposed the application of radium selective crown ethers for direct determination by liquid scintillation with beta-gamma discrimination [17]. The main advantage of this method is the combination of a specific extractant and water immiscible scintillator. Depending on the activity concentration and limit of detection required radium can be determined by direct extraction in the scintillator, or after preconcentration, such as coprecipitation or ion exchange. Uranium concentration in surface and ground waters can vary from 0.1 to 500 ppb, which is far above the limit of detection of the modern ICP-MS [22, 23].

The main purpose of the present work is to develop a simple, rapid, and specific analytical procedure with suitable detection limits for the determination of uranium and radium in water samples operating for different activity concentrations and salt content.

Parameter	Specification
Forwarded RF power, W	1300
Guard electrode	
Coolant gas	13.00 L min ⁻¹
Nebulizer gas	1.05-1.20 L min ⁻¹ (optimized daily)
Auxiliary gas	0.95 L min ⁻¹
Sample uptake	0.10 mL min ⁻¹
Nebulizer	Self aspirating microconcentric PTF
Spray chamber	Double pass cooled to 1 °C
Sampling cone	Nickel–1.1 mm orifice
Skimmer cone	Nickel–0.8 mm orifice
Runs	4-6
Passes	4
Mass resolution, m/ Δ m	300

Table 1.instrumental parameters of the ICP-MS for the determination uranium.

2 Experimental

Instrumentation

A double focusing high resolution ICP-MS instrument (ELEMENT 2, Finnigan MAT, Bremen, Germany) is used for mass spectrometry of uranium. The typical working conditions are presented in Table 1. The instrument sensitivity is daily optimized for maximal response of 120 000 cps for 238 U using a standard solution with concentration 1 ng g⁻¹. The grounded guard electrode positioned between the load coil and the ICP torch, attenuate the plasma potential and molecular based interferences [24]. In addition it could improve the sensitivity of the system by about a factor of 10 [25].

Liquid scintillation alpha spectrometry of radium is performed by means of four PERALS® 8110 (ORDELA, Inc.) spectrometers connected to the Spectrum MasterTM 920-8 - ORTEC analogue-to-digital converter coupled to a PC system [26].

Reagents

The extractive scintillator cocktail RADAEX is purchased from ETRAC. Standard solution of 238 U is delivered by AEA Technology UK, 226 Ra and 133 Ba standard solutions are purchased from NIST. All the chemicals and reagents used are of analytical grade. The water used is deionised Milli-Q 18 M Ω .cm.

Sample material

The analytical procedures for determination of uranium and radium in waters are applied to sample material in the frame of the proficiency test "Determination of radium and uranium radionuclides in water" organized by IAEA-Vienna. Two standard solutions of ²²⁶Ra and natural uranium used for the preparation of the synthetic samples are analyzed (Table 2) along with four natural and four synthetic waters samples with various activity concentration and salt content.

Activity concentration and limit of detection

²³⁸U activity concentration is calculated following the equation:

$$A_U = m_U \cdot A_{SU}, \quad Bq \ kg^{-1} \tag{1}$$

where:

 m_U – Uranium concentration measured by ICP-MS, kg kg⁻¹

 A_{SU} – Uranium specific activity, Bq kg⁻¹

Calculation of ²²⁶Ra activity concentration:

$$A_{Ra} = \frac{N_{nRa}}{\eta \cdot m \cdot Y \cdot t}, \quad Bq \ kg^{-1}$$
⁽²⁾

where:

 N_{nRa} – radium peak net counts

 η – detector counting efficiency

m – sample mass, kg

Y-chemical yield

t – measurement time, sec

The instrument detection limit of ICP-MS is estimated using the Method 6020 approach [23] recommended by EPA.

²²⁶Ra limit of detection is calculated for each particular sample using the Currie's formula [27]:

$$L_{D} = \frac{2.71 + 4.66\sqrt{B}}{\eta \cdot m \cdot Y \cdot t}, \quad Bq \ kg^{-1}$$
(3)

where B – blank counts, cps

The combined uncertainty is estimated according to the uncertainty propagation law [28].



Fig. 1. Flowchart of the radium preconcentration scheme.

Analytical procedures

<u>Uranium</u>: The samples for uranium determination are acidified with HNO₃ and measured directly by ICP-MS. An appropriate set of 238 U standards are used for calibration and 209 Bi in concentration 1 ng g⁻¹ is used as internal standard. The samples with high matrix are diluted to a salt content of 0.05 %.

Radium: The analytical scheme for ²²⁶Ra determination is adapted form McDowell and McDowell [17]. The procedure is based on coprecipitation of radium with barium sulphate, transformation to carbonate, dissolution of the carbonate and extraction in water extractive scintillation cocktail RADAEX. The extractive scintillator contains high molecular weight neo-carboxylic acid and dicyclohexano-21-crown-7 in the molar ratio 2:1 and separates radium from barium, strontium, calcium and uranium by factors of 9, 12, 58 and 6×10^6 respectively [17]. Fig. 1 shows the stages of the radium preconcentration procedure. To the aqueous sample of 100 - 500 mL depending on the expected activity range 10 mg of barium carrier and 30 Bq of ¹³³Ba are added. The solution is acidified with HCl and heated at 80°C under stirring for an hour. Barium sulphate is precipitated with concentrated H_2SO_4 and solution is cooled in ice bath to settle the precipitate. After the supernatant is decanted, the precipitate is washed and boiled with saturated K₂CO₃ solution. The resulted carbonates are separated and dissolved in diluted HNO₃ evaporated and finally redissolved in water. The pH is adjusted between 10 and 12 and the radium extracted with RADAEX and counted on PERALS liquid scintillation spectrometer. The samples with appropriate activity concentration and salt content are directly extracted in RADEAX at V_0/V in the range from 1/6 to 1/10. Fig. 2a presents ²²⁶Ra spectrum collected immediately after the separation and Fig. 2b in secular equilibrium with radium descendants. The yield tracer ¹³³Ba is used to determine the chemical yield in the precipitation and transformation steps, while the yield of the extraction step is evaluated by doping the samples with 226 Ra. Typical total yields are between 73 % and 90 %.

3 Results and Discussion

The information for the sample type, salinity and activity concentrations is presented in Table2. The activity concentrations measured are compared with the target values at 95 % level of confidence.

The reliability of the analytical procedures has been estimated by u-test at 67 % confidence level, Fig. 3. Bellow u = 1.64 the result is considered to be not significantly different from the target value. Between 1.64 and 1.96 the result could not be significantly different and might require more data to support conclusion. Between 1.6 and 2.58 the conclusion whether the results differ can not be done. Between 2.58 and 3.29 the results could be significantly different and more measurements are required to support the conclusion. Above 3.29 the results are significantly different [5, 29]. All the results have u-test value bellow 1.96, and most bellow 1.64 and we can conclude the analytical methodologies applied for the determination of radium and uranium showed very good reliability.

The limit of detection (LD) of radium for sample size 250 mL and counting time up to 400 000 seconds is estimated to be 2.3×10^{-4} Bq kg⁻¹. The instrument detection limit

(IDL) for ICP-MS highly depends on the operational conditions of the instrument used and it has been found to be in the range from 0.4 to 0.8 fg g⁻¹ for ²³⁸U. The LD is evaluated from IDL taking into account the dispersion of the blank, and the dilution factor and the overall limit of detection for uranium is 3.5×10^{-8} Bq kg⁻¹.



Fig. 2. ²²⁶Ra spectra counted immediately after the separation (a) and in secular equilibrium with the radium descendants (b)

^a IAEA consensus values are calculated as robust mean from all the reported results and robust SD. In the parentheses the number of Table 2. ²³⁸U, total uranium and ²²⁶Ra content at 95 % confidential level. laboratories is given.

Sample	Salinity	²³⁸ U reference	²³⁸ U measured	U reference	U measured	²²⁶ Ra reference	²²⁶ Ra measured
code	(g kg ⁻¹)	activity	activity	concentration	concentration	activity	activity
))	(10 ⁻³ Bq kg ⁻¹)	(10 ⁻³ Bq kg ⁻¹)	$(\mu g g^{-1})$	(μg g ⁻¹)	$(10^{-3} \mathrm{Bq}\mathrm{kg}^{-1})$	(10 ⁻³ Bq kg ⁻¹)
IAEA-419	0.67 (S)	31 ± 2	27 ± 16.4	2.50 ± 0.16	2.19 ± 1.35	0.82 ± 062	1.79 ± 1.06
IAEA-421	0.67 (S)	41 ± 2	36 ± 7.2	3.30 ± 0.16	2.91 ± 0.58	55.49 ± 0.74	56 ± 9
IAEA-423	0.67 (S)	238 ± 2	212 ± 42.4	19.17 ± 0.19	17.17 ± 3.43	8690 ± 280	$10\ 840\pm 2\ 150$
IAEA-424	0.52 (N)	$0.47\pm 0.47~(41)^a$	0.079 ± 0.016	$0.039 \pm 0.039 (41)^{a}$	0.0064 ± 0.0013	$54 \pm 52 \ (57)^{a}$	26.7 ± 4.7
IAEA-425	29.6 (N)	$6.3 \pm 0.34 \ (38)^{a}$	6.4 ± 1.2	$0.49 \pm 0.26 \; (38)^{a}$	0.518 ± 0.097	$310 \pm 240 \ (49)^{a}$	280 ± 48
IAEA-426	115 (N)	$26 \pm 14.4 \ (47)^{a}$	28.9 ± 5.8	$2.01 \pm 1.12 \ (47)^{a}$	2.34 ± 0.47	$6500 \pm 5400 (59)^{a}$	$6\ 690 \pm 1\ 140$
IAEA-428	3.7 (N)	$58 \pm 32 (61)^a$	67.9 ± 13.6	$4.6 \pm 2.8 \ (61)^{a}$	5.51 ± 1.10	$3600 \pm 2200 \ (76)^{a}$	$4\ 190\pm 690$
IAEA-430	90 (S)	109 ± 2.6	98 ± 19.6	8.81 ± 0.20	7.94 ± 1.58	3050 ± 100	$3\ 274\pm530$
S-22	I	I	I	I	I	(50200 ± 1560) .10 ³	(56478 ± 9793) .10 ³
S-68	I	(486 ± 3) 10 ³	(405.05 ± 81.02) $.10^3$	39200 ± 240	32798 ± 6560	I	I

S – synthetic sample N – natural sample

Fast determination of uranium and radium in waters





Fig. 3. u-Test estimating reliability of the analytical procedures.

The procedure for sample preparation of uranium requires relatively short time. A set of eight samples can be prepared within one hour and the analysis by ICP-MS takes 3 minutes per sample. In contrast, the standard radiochemical separation of uranium, followed by alpha spectrometry demands as a rule more than 36 hours. Radium preparation takes more time. A skilled analyst can run 10 samples simultaneously which preparation takes from 6 to 12 hours depending on the sample size and salt content. Since the speed of the radium analysis is limited by the sample counting in practice preparation of more than 4-6 samples daily is not necessary.

The used analytical procedures are simple and accurate. The limits of detection are appropriate for routine monitoring of the radium and uranium in all kind of water samples.

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