

RADIUM ISOTOPES DETERMINATION IN ROCK SAMPLES USING ALPHA SPECTROMETRY

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ABSTRACT. In the present paper different methods for radium isotopes determination in the environmental samples are discussed. In the framework of IAEA Contract No 11298 the new procedure is adapted and applied for more precise determination of the Radium isotopes concentration in soil and rock materials. The radiochemical procedure is based on fusion technique for rapid determination of Ra-226 described by R.Bojanowski at all, 2002. The isotope of Ba-133 was used for determination of the chemical yield. The main steps in the procedure described and discussed in this study are: 1) total sample decomposition by fusion with Lithium Metaborate; 2) dissolution in Na₂SO₄ and citric acid solution; 3) separation of Barium and Radium by co-precipitation as sulfate; 4) source preparation on 0.1 µm pore size filter by filtration of the fine Ba/Ra -sulfate precipitation; 5) alpha spectrometry of the source for ²²³Ra, ²²⁴Ra and ²²⁶Ra isotopes determination immediately after source preparation to avoid Radium daughters growth 6) ¹³³Ba yield determination by gamma spectrometry.

The procedure was tested successfully on IAEA-reference materials. Large number analyses for Radium isotopes content in samples of the newly developed reference material from the region of the village of Eleshniza were performed. The proposed material had been previously tested for uranium isotopes content and has shown acceptable homogeneity. The results from radium isotopes determination show homogeneity in Ra concentration and dis-equilibrium with parent uranium isotopes making this way the proposed Eleshniza material interesting reference material for naturally occurring uranium series.

ОПРЕДЕЛЯНЕ НА ИЗОТОПИТЕ НА РАДИЯ В СКАЛНИ МАТЕРИАЛИ С ИЗПОЛЗВАНЕ НА АЛФА-СПЕКТРОМЕТРИЯ

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В доклада се дискутират различни методи за определяне на изотопите на радия в проби от околната среда. Подробно е изложена новата адаптирана аналитична процедура за по-прецизно определяне на изотопите на радия в почвени и скални проби, разработена в рамките на Договор No 11298 с МААЕ. Радиохимичната методика се базира на използването на техниката на стопилка, следвайки R.Bojanowski at all, 2002. За определяне на химическия добив се използва трасер ¹³³Ba. Основните стъпки в методиката, разглеждани и дискутирани в това изследване са: 1) пълно разтваряне на пробата като стопилка с литиев метаборат; 2) разтваряне на стопилката в разтвор на Na₂SO₄ и лимонена киселина; 3) разделяне на радия и бария посредством сътаяване като сулфати; 4) изготвяне на източник чрез филтриране на Ba/Ra сулфатни микрочастици през филтър с размер на порите 0.1 µm; 5) алфа-спектрометрия за определяне на ²²³Ra, ²²⁴Ra и ²²⁶Ra изотопи непосредствено след изготвяне на източника, за да се избегне израстването на дъщерните изотопи на радия; 6) гама-спектрометрия за измерване активността на трасера ¹³³Ba за оценка на химическия добив. Методиката е тествана успешно върху референтни материали на МААЕ. Бяха извършени значителен брой анализи за съдържанието на изотопите на радия в предлагания нов референтен материал от района на Елешница. Материалът от Елешница, тестван успешно за хомогенност по отношение на урана в едно предишно изследване показва и добри резултати по отношение съдържанието на изотопите на радия. Нарушеното равновесие между съдържанието на уран и радий в материала го прави особено интересен като референтен материал за радиоактивните семейства на природния уран.

Introduction

Radium was discovered in 1898 by Mme.Curie in the pitchblende or uraninite of North Bohemia where it occurs. Radium is a naturally-occurring metal that is almost ubiquitous in soils, water, geologic materials, plants, and foods at low concentrations. The utilization of radium, uranium, and fossil fuels has resulted in the redistribution of radium in the environment by way of air, water, and land releases. The concentration of radium in natural water is usually controlled by adsorption-desorption reactions with minerals and rocks and by the solubility of radium-containing minerals. In addition, radium is constantly being produced by the radioactive decay of its precursors, uranium, and thorium (Table 1):

Table 1.

Characteristics of Radium isotopes

Isotope	Direct parent	Half life	Decay mode	Energy (MeV)
Ra-223	Th-227	11.4 d	alpha	5.61 5.72
Ra-224	Th-228	3.66 d	alpha	5.69
Ra-226	Th-230	1620 y	alpha	4.78
Ra-228	Th-232	5.75 y	beta	0.046

Radium does not degrade other than by radioactive decay at rates which are specific to each of four naturally-occurring

isotopes. The concentrations of radium-226 and radium-228 in drinking water are generally low, but there are specific geographic regions where high concentrations of radium occur due to geologic sources. Radium may be bioconcentrated and bioaccumulated by plants and animals, and it is transferred through food chains from lower trophic levels to humans.

Another potential source of atmospheric radium is particulate matter created by uranium mining and milling operations. The importance of this radioactive element is determined of its progeny Radon. Radon is gas and also radioactive. Other potentially hazardous substances in the tailings are selenium, molybdenum, uranium, and thorium. The problem with conserving of former mines is ubiquitous.

Our investigations on similar objects – on former uranium mines in the USA EPA's data from two former uranium mines in the USA - *Fremont National Forest* (White King) and *Lucky Lass Uranium Mines*. The data show that there is a tendency of higher activities of Ra-226 in overburden pile (i.e. disequilibrium) than these of uranium isotopes, although in this case concentrations of radionuclide are lower than ours.

Table 2.

Concentrations of ^{234}U , ^{238}U and ^{226}Ra in the regions of USA former uranium mines, Rep.1999

Radionuclide	White King Protore Pile (0.8-3.0m)	White King Overburden Pile (0.8-3.0m)	Lucky Lass Overburden Pile (0.8-3.0m)
	(Bq/g)	(Bq/g)	(Bq/g)
U-234	2.03	0.85	0.07
U-238	2.00	0.75	0.08
Ra-226	1.36	1.97	0.07
Ra-228	0.03	0.04	0.04

The former uranium mines Eleshnitsa are located in the South-West Bulgaria in the valley of the river Mesta, Fig.1. According to the IAEA data from TECDOC-865, Vol.2 (1996), p.50, the waste rock deposits in the former mines of Eleshnitsa are estimated in 15.3 ha of area and 2.9x10⁶ tons. This huge area became a potential hazard for people's health in the region after closing the mines.

Fig. 1. Map of the region of Eleshnitsa

There are four principal ways (or exposure pathways) that the public can be exposed to the hazards from this waste. The first is the diffusion of radon gas directly into indoor air if tailings are misused as a construction material or for backfill around buildings. When people breathe air containing radon, it increases their risk of developing lung cancer. Second, radon gas can diffuse from the piles into the atmosphere where it can be inhaled and small particles can be blown from the piles where they can be inhaled or ingested. Third, many of the radioactive decay products in tailings produce gamma radiation, which poses a health hazard to people in the immediate vicinity of tailings. Finally, the dispersal of tailings by wind or water, or by leaching, can carry radioactive and other toxic materials to surface or ground water that may be used for drinking water.

Results and discussion

The methods for determination of radium can be classified into two categories:

- Based on direct measurement of Radium isotopes as such – alpha/beta/gamma spectrometry or ICP-MS analysis;
- Based on its decay products Rn-222, Po-218, Po-214 and Bi-214.

The second category is the most popular because the methods offer both high sensitivity and specifics (radon emanation) or require little effort for sample preparation and measurement. However, they are time consuming as samples need to lay in wait for the decay products to build up. Usually, the samples are kept in gas-proof vessels for a month or more during which the secular equilibrium within the decay chain is achieved.

The determination of Radium isotopes by alpha spectrometry for samples of rock material is described below. The method for Radium isotopes determination was applied both to IAEA reference (Soil 5 and IAEA 315) materials and rock material collected around former Uranium mines of Eleshnitsa:

The radiochemical procedure is based on fusion technique for rapid determination of Ra-226 described by R.Bojanovski et al, 2002. The isotope of Ba-133 was used for determination of chemical yield.

An aliquot of about 0.2 g of previously ashed material Eleshnitsa is placed in Pt crucible and Ba-133 tracer is added. One gram Lithium Metaborate (five times the weight of sample) is added and mixed with the sample. This mixture is heated on the flame of spirit burner to dryness, avoiding spattering. The crucible is covered with a lid and put in a crucible oven until a homogenous melt is obtained with no visible particles inside. The sample is heated at about 800°C for 20 minutes.

After this the crucible is removed, cooled and a pinch (~0.1 g) of NaBr is added. The heating is resumed until the contents turn to liquid. When the melt assumes a ball-like shape, it is rolled gently around the crucible walls until all fine beads of molten material that may adhere to them combine with the bulk of the melt. Then quickly it is transferred to the beaker containing 50 ml of the dissolving solution – combined solution of Na₂SO₄ and citric acid. This solution is stirred vigorously with teflon stirring bar and a portion of 50ul of seeding suspension of BaSO₄ is added immediately. The stirring continues another 5 minutes and the second portion of 50ul of seeding suspension of Ba₂SO₄ is added. The process of stirring is maintained to the total dissolution of the melt. In our case it is about 40 minutes.

13.72 % Al₂O₃; 3.17 % K₂O; 1.46 % Fe₂O₃. On Fig.3 is given typical alpha spectra of the Eleshnitsa material.

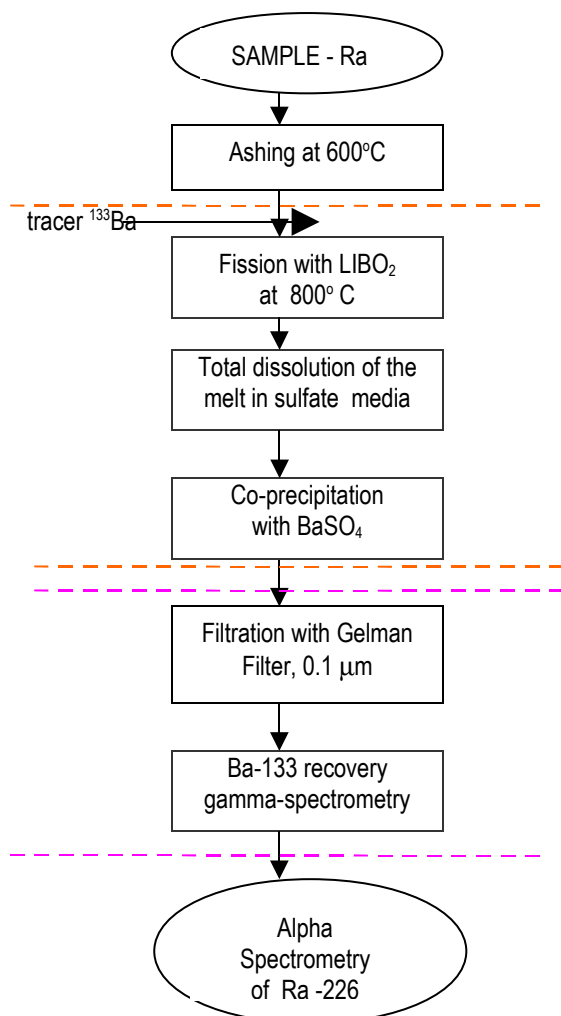


Fig. 2. Schema of the radiochemical procedure

Then the precipitate is filtrated by vacuum filtration system on a membrane filter with pore size of 0.1 µm (Gelman filter). The beaker and filter chimney are washed with bi-distillated water followed with 80% ethanol and all washes are passed through the filter.

Then the so prepared source of Ba(Ra)SO₄ is given consequently for alpha and gamma measurements. The radiochemical procedure can be summarized in the scheme, given on Fig.2.

Alpha spectrometry was performed by ORTEC Octete Alpha Spectrometric system equipped with 8 Ortec ULTRA-SA™ low background ion implanted detectors with 300mm² active area. The alpha spectrometric system was obtained under IAEA TCP RER 2/003. More information about the features of the spectrometric system are given in Veleva (1998).

The measured total system resolution FWHM for ²⁴¹Am 5.486 MeV alphas is close (or even lower) to 19keV for 4cm source to detector distance for all detectors. Energy calibration as well as efficiency calibration for one of source geometry (co-ppt. Source) is done by mixed radionuclides standard containing ²³⁸U, ²³⁴U, ²³⁹Pu and ²⁴¹Am with known activity, and for geometry of electroplated sources the efficiency calibration is estimated by Amersham ²⁴¹Am standard. The experiments were performed on different aliquots of already prepared "Eleshnitsa reference material". The material is close to composition of rock with main components: 73.79 % SiO₂;

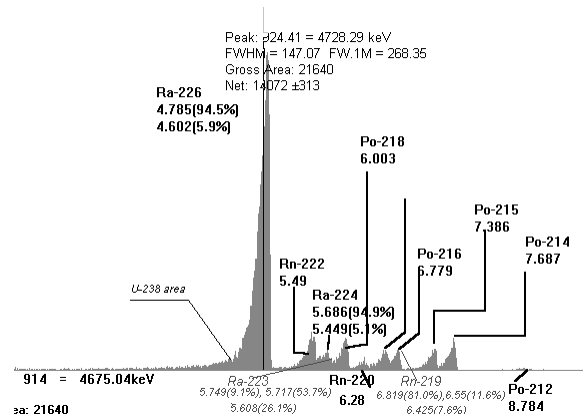


Fig. 3. Alpha spectrum of one of the Eleshnitsa samples

The procedure has the following important advantages:

- It is really very simple and fast – the fission of the sample with lithium Metaborate, the follow dissolving of the flux and preparing the alpha source take only 3 hours;
- The measurement of sample is carried out immediately after that. In this way there is no time for ingrow of daughter's products that could contaminate the detector and alpha specter itself;
- The technique is environmental friendly – no concentrated acids are used. In comparison with the digestion technique used in uranium determination procedure, where Hydrofluoric acid (that is very toxic) is used.
- The last but not least in importance, the procedure is cheap. Except of using of Lithium Metaborate, that is relatively expensive because of special technique for its purification, no special materials are used.

The challenges in Ra determination by α-spectrometry, compared to the alpha spectrometry of other radioactive elements as Uranium, Plutonium etc. is due to two main reasons: First of all the chemical yield is determined by other technique (gamma spectrometry of ¹³³Ba) and second – fast growth of radium daughters. Therefore alpha spectrometry of Radium require:

- a) precise efficiency calibration - in our set of measurements the systematic error is estimated as < 7%
- b) reproducible geometry - measurements at least in 2 chambers to minimize error
- c) to obtain precise results for all alpha emitting Radium isotopes several measurements for a sample are needed- at least one immediately after co-precipitation and 2nd - a month later
- d) for ²²⁴Ra determination if $t_{\text{meas}} > 0.01 \cdot T_{1/2}$, or for times of 3200s and more, a decay correction is applied:

$$A_s = A_n f, \text{ where } f = \lambda t / (1 - \exp(-\lambda t))$$

- e) ²²⁴Ra and ²²³Ra close energies leads to peaks overlay - if their activities are similar determination by daughters Po isotops is applied
- f) the possible contamination of the detector and vacuum chamber requires regular background measurements.

On Fig.3 is given an example of the detector contamination by recoil atoms and consequential clean up by decay in the

energy regions of ^{222}Rn , ^{218}Po , ^{214}Po . If ^{226}Ra contamination occurred, it will increase the Detection Limit for the detector life time.

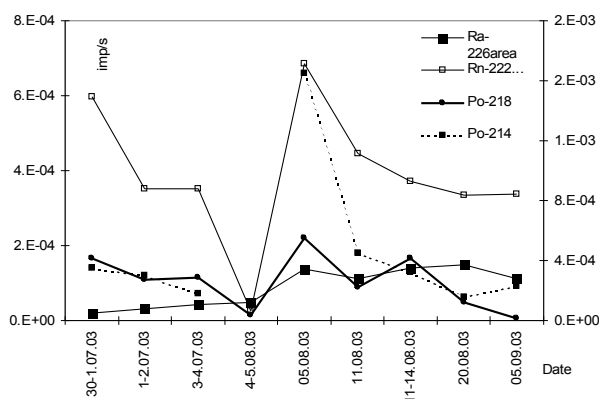


Fig. 4. Background variation of the detector 3. The values (in imp/s) for ^{226}Ra and ^{222}Rn energy regions are on the left axes and ^{214}Po , ^{218}Po on the right

The obtained results for ^{226}Ra concentration in more than 15 sub-samples from the Eleshnizta reference material have proved the reproducibility and reliability of the presented method, see Fig.5. The measured concentrations are comparable to those obtained by gamma spectrometry of the ^{226}Ra daughters and by LSC.

Table 3.

Comparison of the results for Ra-226 by LCS, gamma- and alpha-spectrometry in kBq/kg

Sample No	LCS	Alpha-spec	Gamma-spec
1	10.3 ± 1.3	12.8 ± 2.2	13.9 ± 4.5
2	12.4 ± 0.6	12.3 ± 0.9	13.4 ± 4.7
3	12.8 ± 0.9	13.6 ± 1.2	14.2 ± 3.5

The results from analyses showed disequilibrium with uranium concentrations previously determined in the same material. When for uranium content (^{238}U , ^{234}U) received an average concentration of 2.0 Bq/g, for ^{226}Ra we received 12Bq/g. Large number analyses for Radium isotopes content in samples, previously tested for uranium isotopes content, show acceptable homogeneity for both elements.

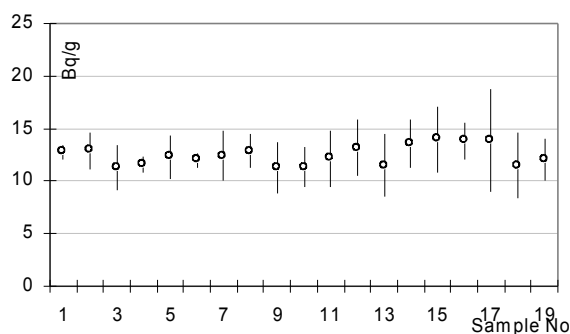


Fig. 5. ^{226}Ra concentration and 1 uncertainty in Eleshnizta samples

Conclusion

The developed procedure proved as appropriate (suitable) for alpha emitting Radium isotopes determination in soil, rock and other samples. The disequilibrium between parent U isotopes and daughters Radium isotopes in Eleshnizta material make it very interesting as reference material for testing different analytical techniques for naturally occurring uranium series determination.

Reference

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