

COMPARISON OF DETERMINING ^{228}Ra VIA LSC AND GAMMA SPECTROMETRY IN MINERAL WATERS

Marta Vršková^{1,2} • Jana Merešová¹ • Alena Belanová¹ • Martina Ferenceiová³

ABSTRACT. ^{228}Ra is one of the most toxic natural radioisotopes; therefore, its measurement in water samples is the objective of our study. We compare the determination of ^{228}Ra via liquid scintillation counting (LSC) and gamma spectrometry in selected mineral waters. Radium was separated and concentrated from the water by barium sulfate precipitation. The scintillator was then added and the sample was measured by a liquid scintillation analyzer. For determining ^{228}Ra by gamma spectrometry, samples were preconcentrated by evaporation from volumes of 6 L to 450 mL by adding nitric acid or by evaporating to a dry residue. The treated sample was measured in a Marinelli beaker or in an evaporated residue by gamma spectrometry. We tested bottled mineral waters samples since we expected the increased content of radium to be dependent on the origin of the mineral water.

INTRODUCTION

For many years, the content of the radionuclide ^{228}Ra in drinking water was not systematically monitored in Slovakia and believed not to be significant from the radiohygienic point of view. The International Commission on Radiological Protection (ICRP) in 1966 reappraised the doses for ingestion and inhalation, and according to this assessment, the radiotoxicity of ^{228}Ra increased. ^{228}Ra belongs to a group of the most toxic radionuclides, and its highest level in the regulations of the Ministry of Health of the Slovak Republic (2001) is half that of ^{226}Ra (Table 1). The World Health Organization (2004) regulation for Drinking Water Quality recommends a reference value of 0.1 Bq/L for ^{226}Ra .

Table 1 Highest permissible levels of activity of radium isotopes in drinking, mineral, and baby water (Ministry of Health of Slovak Republic 2001).

Radionuclide	Activity in baby water (Bq/L)	Activity in natural mineral table water and other table water (Bq/L)	Activity in drinking and tap water (Bq/L)
^{226}Ra	0.2	1.9	0.6
^{228}Ra	0.1	0.7	0.3

^{228}Ra is pure beta emitter and a member of the thorium decay chain and is the first daughter product of ^{232}Th . There are several possible methods for determining ^{228}Ra . One method for detection is to measure the daughter product ^{228}Ac after stabilization of radioactivity equilibrium (~60 hr). ^{228}Ac emits several electrons and photons with different energies (see Table 2).

We compared 2 methods considering our accessible laboratory equipment and devices: standard gamma spectrometry and liquid scintillation counting (LSC). Results of this comparison are discussed below. For testing samples, we chose bottled mineral and healing waters. (The healing waters are not meant for everyday use; they are used in regulated doses for improving health in spas.) A higher radioactivity level was expected due to the increased mineralization in these types of waters.

¹Water Research Institute, Nábr. L.Svobodu 5, 81249 Bratislava, Slovakia.

²Corresponding author. Email: marta_vrskova@vuvh.sk.

³Faculty of Chemical and Food Technology STU, Radlinského 9, 81237 Bratislava, Slovakia.

Table 2 Basic characteristics of radionuclides with main emissions listed (Debertin and Helmer 1988).

Radionuclide	Half-life	Radiation type	Energy (% probability)
^{226}Ra	1620 yr	α	$E_{\alpha} = 4784.5 \text{ keV (94.55\%)}$
		α	$E_{\alpha} = 4601.9 \text{ keV (5.55\%)}$
		γ	$E_{\gamma} = 186.2 \text{ keV (3.28\%)}$
^{228}Ra	5.7 yr	β	$E_{\beta, \text{max}} = 38.9 \text{ keV (100\%)}$
^{228}Ac	6.13 hr	β	$E_{\beta, \text{max}} = 1168.1 \text{ keV (32\%)}$
		γ	$E_{\gamma} = 911.1 \text{ keV (27.7\%)}$
		γ	$E_{\gamma} = 969.1 \text{ keV (16.62\%)}$

EXPERIMENTAL

Gamma Spectrometry

One important advantage of gamma spectrometric analysis is its ability to determine several gamma-emitting radionuclides together without a preceding chemical separation. It is the one of the most sensitive and precise methods for measuring radioactivity.

The radionuclide ^{228}Ra itself does not emit a gamma quantum suitable for determination via gamma spectrometry, but its decay product ^{228}Ac emits several photons with various energies. After 72 hr of stabilization of the radioactive equilibrium, it is possible to use ^{228}Ac for determining ^{228}Ra (Hanslík et al. 1992).

Due to the very low concentration of Ra in water, preconcentration of the samples is required. We compared 2 different techniques of sample preparation for gamma spectrometry determination. The mineral waters were concentrated from volumes of 5–6 L. The first technique was the preconcentration via gradual evaporation, with the addition of HNO_3 (to pH 2) to prevent precipitation of solid matter, to 450 mL in a Marinelli beaker. The second method was the evaporation to dry residue. After evaporation, the dry residue was burned with foil and placed in the measuring vial.

After 3 days, when the radioactivity equilibrium had been established, the samples were measured using the gamma spectrometer EG&G ORTEC GEM-30195 with the HPGe detector placed in a low-level background shield. The measurement time was 200,000 s, and the background was measured before and after running the sample. Calibration was done using a certified solution of $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ and these standard solutions were handled using the same techniques as the samples.

Liquid Scintillation Counting (LSC)

The advantage of the liquid scintillation technique is the simultaneous determination of α and β particles (Chalupnik and Lebecka 1993; Wallner 2002). In the software program QuantaSmart™, α and β particles are separated by color (α particles are blue, β particles are green).

The mineral waters have various levels of mineral substances. We used a classic method for preconcentrating Ra from the samples based on the method of Chalupnik and Lebecka (1993). Ra was preconcentrated from the water (1 dm^3) with a Ba carrier and Pb, and the precipitate was dissolved in EDTA. Ra was separated from Pb by coprecipitation of Ra and Ba as sulfates. The Ba and Ra sulfate precipitation was then mixed with the scintillation cocktail Ultima Gold™ (PerkinElmer, USA).

After 30 days, the samples were measured using the liquid scintillation analyzer Tri-Carb 2900TR, and data processing was carried out using QuantaSmart software. The ^{228}Ra concentration was calculated using the calibration. The time of measurement was 1 hr. The calibration curve (Figure 1) was made by using the certified solution of $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ and measured after 30 d in the same conditions as the samples.

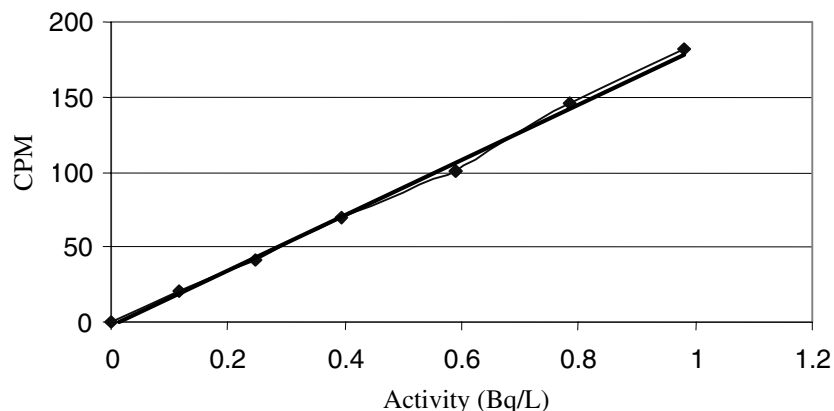


Figure 1 Calibration curve for ^{228}Ra using the LSC method

RESULTS AND DISCUSSION

Comparison of Tested Methods

Table 3 presents the main characteristics (volume of sample, time of measurement, and limit of detection) for the 2 methods used. Gamma spectrometry is more time consuming and requires larger volumes of sample compared to the LSC method. The limit of detection for both methods is sufficient according to the ^{228}Ra limit of concentration given by the regulations.

Table 3 Comparison of both methods in determining the activity concentration of ^{228}Ra .

Method		Volume of sample (L)	Time of measurement (s)	^{228}Ra limit of detection (Bq/L)
Gamma	Marinelli beaker	4.9–6.0	200,000	0.013
	Evaporation residue	6.0	200,000	0.004
LSC		1.0	1200	0.074
			3600	0.008

Table 4 presents the uncertainties of ^{228}Ra measurements for both methods. Method B was used for the calculation of uncertainty.

Activities in Mineral Waters

The activity concentration of ^{228}Ra was determined in 10 bottled mineral and healing waters accessible in Slovakia. Results determined using gamma spectrometry and LSC are presented in Table 5 (95% confidence level). The ^{228}Ra activity concentration varied from 0.03 ± 0.02 Bq/L in the mineral water Korytnica to 1.08 ± 0.14 Bq/L in the healing water Vincentka. The highest permissible level of concentration of ^{228}Ra in natural mineral table water and other table water (Table 1) was exceeded only by the healing water Vincentka.

Table 4 Uncertainty of ^{228}Ra determinations.

Method	Uncertainty of ^{228}Ra determination		
	Range of activity concentration (Bq/L)	Expanded uncertainty ($k = 2$)	
Gamma spectrometry	<0.2	911 keV	969 keV
	0.2–0.3	>100%	>100%
	0.3–0.4	50%	80%
	0.4–1.0	30%	60%
	>1.0	20%	40%
LSC	<0.1	15%	20%
	0.11–0.40	<100%	
	0.41–1.20	50%	
	>1.20	20%	

Table 5 Volume activities of ^{228}Ra in bottled mineral waters.

Mineral water	Activity concentration of ^{228}Ra (Bq/L)	
	Gamma spectrometry	LSC
Radenska (sparkling)	0.38 ± 0.22	0.43 ± 0.21
Radenska (quiet)	0.19 ± 0.22	0.26 ± 0.15
Čerínska	0.25 ± 0.22	0.44 ± 0.09
Salvator	0.17 ± 0.23	0.25 ± 0.14
Vincentka	0.82 ± 0.28	1.08 ± 0.14
Budiš	0.16 ± 0.05	0.22 ± 0.06
Korytnica	0.05 ± 0.07	0.03 ± 0.02
Kláštorná	0.06 ± 0.09	0.08 ± 0.04
Fatra	0.13 ± 0.09	0.02 ± 0.02
Slatina	0.15 ± 0.07	0.14 ± 0.05

CONCLUSION

Bottled mineral waters were used as real samples with an expected increased activity of ^{228}Ra . Only the healing mineral water Vincentka exceeded the highest permissible level according to Slovak regulations (0.7 Bq/L).

When comparing the results obtained using the gamma spectrometry and LSC methods for determining ^{228}Ra , some differences are clear (Table 5). However, one must consider that these methods are still in development. In the near future, we plan to optimize the measuring conditions for determining ^{228}Ra with simultaneous determination of ^{226}Ra .

REFERENCES

- Chalupnik S, Lebecka JM. 1993. Determination of ^{226}Ra , ^{228}Ra and ^{224}Ra in water and aqueous solutions by means of liquid scintillation counting. In: Noakes JE, Schönhofer F, Polach H, editors. *Liquid Scintillation Spectrometry 1992*. Tucson: Radiocarbon. p 397–403.
- Debertin K, Helmer RG. 1988. *Gamma- and X-ray Spectrometry with Semiconductor Detectors*. Amsterdam: North-Holland. 400 p.
- Hanslík E, Mansfeld A, Filip J, Šimonek P. 1992. Possibility of gamma spectrometry analysis at identification source of contamination sources with the radioactive substances. *Proceedings of the Hydrochémia 1992 Conference*. Bratislava: Academy of Sciences of the Czech Republic. p 292–311. In Czech.
- Ministry of Health of Slovak Republic. 2001. Regulation MZ SR #12/2001. Bratislava: Ministry of Health.

Wallner G. 2002. Determination of ^{228}Ra , ^{226}Ra and ^{210}Pb in drinking water using liquid scintillation counting. In: Möbius S, Noakes JE, Schönhofer F, editors. *LSC 2001, Advances in Liquid Scintillation Spectrometry*. Tucson: Radiocarbon. p 269–74.

World Health Organization [WHO]. 2004. Guidelines for Drinking Water Quality. 3rd edition. Volume 1, Recommendations. Geneva: WHO. URL: http://www.who.int/water_sanitation_health/dwq/gdwq3/en/.