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DETERMINATION OF ^{226}Ra AND ^{228}Ra IN WATER USING LabSOCS EFFICIENCY CALIBRATION SOFTWARE FOR GAMMA SPECTROMETRIC ANALYSIS

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Abstract. *Radium (Ra) isotopes are important from the viewpoints of radiation protection and environmental protection. Radium is routinely analyzed in drinking water. Radium isotopes can be analyzed by different analytical methods based on gamma spectrometric measurements or alpha spectrometry. Modern gamma spectrometry systems are typically operated via computer software applications. In this study, the LabSOCS (Laboratory Sourceless Calibration Software) mathematical efficiency calibration software is used. An improved method was developed to determine radium isotopes from water using gamma spectrometry after micro-coprecipitation as lead (radium) sulfate method for radiochemical separation* ($Pb(Ra)(Ba)SO_4$)*. This method was successfully modified to allow direct determination of* ^{226}*Ra and* ^{228}*Ra by gamma spectrometry. However, large volumes of samples and/or long waiting time (20 days), before radioactive equilibrium is established, are required for accurate* ^{226}*Ra activity concentration determination. The amounts of* ^{226}*Ra and* ^{228}*Ra on the sample were quantified by using gamma spectrometric analysis for its 186 keV gamma emission, 351.9 (*^{214}*Pb), 295.2 (*^{214}*Pb), and 609.3 (*^{214}*Bi), 1764.5 (*^{214}*Bi) and for* ^{228}*Ra can be nonetheless achieved via its daughter nuclide* ^{228}*Ac in 911.2 and 969 keV gamma emission. The radiochemical recovery was 93% and 100% for* ^{226}*Ra and* ^{228}*Ra, respectively. The Minimum Detectable Activities (MDAs) for 8L of sample and a measuring time of 2.3 days for* ^{226}*Ra and* ^{228}*Ra were calculated. The best results were obtained when the herein described method was combined with LabSOCS calculations.*

Key words: *Radium in water, gamma-ray spectrometry, radiochemical procedure, LabSOCS*

1. INTRODUCTION

The ^{226}Ra and ^{228}Ra are the most likely isotopes to be found in drinking water and they are more commonly found in drinking water supplies derived from groundwater where chloride, carbonate and sulphate anions (among others) tend to increase the mobility of radium [1]. In this study, the LabSOCS (Laboratory Sourceless Calibration Software) mathematical efficiency calibration software is used. Methods for the determination of radium isotopes in environmental solids by gamma spectrometry can be obtained by two means, the direct measurement of the principal photopeaks (186 keV in the case of ^{226}Ra), and indirect measurement using the gamma radiation emitting progeny [2]. The advantage of using the direct measurement method, particularly for ^{226}Ra, is that the sample can be prepared and measured immediately without the need for progeny ingrowth.

The disadvantages of this method relate primarily in that the emission probability of this gamma photopeak is quite weak (3.6%), and furthermore by the presence of the interfering primary gamma emission of ^{235}U at 185.7 keV that has a higher photon emission probability of 57%. The energy resolution of currently available HPGe spectrometers is generally considered insufficient to separate the two peaks. If no chemical separation is carried out initially, quantification of ^{226}Ra via the 186.2 keV gamma line must be conducted by attempting to quantify the contribution of the ^{235}U isotope to the doublet peak. In our study, micro-coprecipitation as lead (radium) sulfate method for chemical separation is used.

After the coprecipitation step, the radium isotopes are measured by gamma spectrometry. ^{226}Ra can be determined by gamma spectrometry by exploiting its gamma emission at 186.2 keV. Lower detection limits are achieved by analyzing its daughter nuclides – lead-214 (^{214}Pb) and bismuth-214 (^{214}Bi) – with gamma lines with higher emission probabilities. By sealing a radium source, radon-220 (^{220}Rn) can be contained, and, after 20 days, the radioactive equilibrium of ^{226}Ra with its daughters ^{214}Pb and ^{214}Bi is established.

The direct determination of ^{228}Ra by gamma spectrometry is complicated, since its most important gamma line at 26.4 keV has a very low emission probability of only 1.6 %. An accurate determination of ^{228}Ra can be nonetheless achieved via its daughter nuclide ^{228}Ac. This radionuclide has a gamma line at 911.2 keV with a high emission probability of 26.2 %. The radium source is stored for 30 hours before counting in order to allow for the radioactive equilibrium between ^{228}Ra and ^{228}Ac to be established.

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2. EXPERIMENTAL

2.1. Radiochemical Procedures

The water sample (minimum 7 kg) was weighed into two 5 L glass beakers. A magnetic stirrer was added and the beaker was put on a hotplate stirrer. 0.3 mL of ^{133}Ba tracer was added into each beaker containing the sample for recovery determination. Concentrated H_2SO4 (7 mL per L of sample) was added. Pb(Ra)(Ba)SO4 was precipitated by adding 6 mL of the Pb2+ solution (50 mg/mL) dropwise while stirring and heating the solution at 90°C. The white precipitate appeared in a few minutes. If the precipitate did not appear after 20 minutes of stirring, another 1 mL of Pb2+ solution and 5 mL of conc. H_2SO4 per L of sample were added. The solution was stirred for 3 hours. The stirring was stopped, the stirrer bar was removed and the beaker was covered with watch glass to allow the precipitate to settle down (overnight). The supernatant was decanted to as low a volume as possible. The decanted supernatant was discarded. The precipitate was washed into a 50 mL centrifuge tube with deionized water and then centrifuged at 2500 rpm for 4 minutes. The supernatant was discarded. The precipitate was transferred to a plastic container with 12 mL of deionized water and left under the IR lamp until all of the water evaporated. The plastic container was sealed using liquid glue and left to rest for three days in order to allow for ^{228}Ac ingrowth. The samples were measured for 2.3 days on a coaxial-type gamma spectrometer in order to determine ^{226}Ra via daughters. After 20 days, the samples were re-measured, each for 2.3 days, on the same coaxial-type gamma spectrometer.

2.2. Instrumentation

All samples were prepared in a disc plastic container with the same size of about 3.2 cm in diameter to obtain the similar counting geometry. Gamma spectrometry based on a high-purity germanium detector was used. The HPGe detector has a Full Width at Half Maximum (FWHM) of 1.9 keV for ^{60}Co gamma energy line at 1332 keV and is operated with the Canberra Genie 2000 software for gamma acquisition and analysis. ^{226}Ra was then quantified by gamma counting for its 186 keV gamma emission, 295.2 (^{214}Pb), 351.9 (^{214}Pb), 609.3 (^{214}Bi), 1764.5 (^{214}Bi). For ^{228}Ra 338.3 gamma emission, 911.2 and 969 keV was used. The gamma spectrometer was calibrated using a standard source with known radionuclides for energy calibration and LabSOCS software for efficiency calibration curve was used. The analysis of the spectra with the known amounts of ^{226}Ra and ^{228}Ra allowed the determination of peak widths, peak resolution and counter efficiencies at different energies and it allowed the determination of counter precision, accuracy and recovery. Two samples are spiked with known amounts of ^{226}Ra and ^{228}Ra and three preliminary samples are spiked with known amounts of ^{226}Ra. All five samples were counted directly in the system with a suitable counting time.

2.3. Description of samples

In the beginning, the proposed radiochemical method was tested with three water samples (DG1, DG2 and DG3) prepared by spiking 4.5 L of tap water with different amounts of a ^{226}Ra standard solution and finally adding a known amount of ^{133}Ba tracer. The final ^{226}Ra activity concentrations in the spiked tap water samples were estimated to vary from 0.14 to 0.37 Bq/L. The objectives of this part were to estimate whether a direct determination of ^{226}Ra in combination with LabSOCS software is a viable option for routine analysis and to estimate the radiochemical recovery of ^{133}Ba (^{226}Ra and ^{228}Ra). In the second part, a set of 2 water samples, which are denoted as GS1 and GS2 in the tables 2 and 3 that were prepared by spiking 10 L of deionized water with known amounts of ^{226}Ra and ^{228}Ra standard solutions were analyzed. Contrary to the preliminary test, ^{228}Ra standard solution was at this stage also added to the samples since it is well known that the gamma emission(s) of its daughter ^{228}Ac allow an accurate determination of ^{228}Ra by gamma spectrometry. This part was conducted similarly to an intercomparison run, in the way that the analyst received the samples without knowing their reference activities. For each sample, two aliquots of ca. 7.5 L were taken and analyzed by the radiochemical method described above.

2.4. Determination of Radium concentration

The specific activity (in Bq kg-1), $A_{E\gamma,i}$ of a radionuclide i and for a peak at energy E_γ, is given by [3]:

$$A_{E\gamma,\,i} = \frac{NP}{t_c I_\gamma(E_\gamma)\varepsilon(E_\gamma)M} \qquad (1)$$

where NP is the number of counts in a given peak area corrected for background peaks of a peak at energy E_γ, ε (E_γ) the detection efficiency at energy E_γ, t is the counting lifetime, I_γ (E_γ) the number of gammas per disintegration of this nuclide for a transition at energy E, and M the mass in kg of the measured samples. The procedure is based on micro-coprecipitation as lead (radium) sulfate for chemical separation. The yield of the procedure is determined in each sample by adding a ^{133}Ba radioactive tracer. The 356.0 keV γ-ray of ^{133}Ba is used for yield determinations. The highest energy γ-ray from ^{133}Ba is 383.8 keV, which does not interfere with the energies 911 keV from ^{228}Ac.

$$Y_s = \frac{\text{Final mass of barium sulphate}}{\text{Initial mass of barium sulphate}} \qquad (2)$$

where Y_s is the chemical yield determined for the sample in equation (2).

The calculation of errors is determined by the use of the following equation [4]:

$$\sigma = \frac{\sqrt{N}}{t} = \sqrt{(\frac{N}{t^2})} = \sqrt{\frac{r}{t}} \qquad (3)$$

where r is the net count rate.

We are interested in subtracting one count from another (gross counts minus background counts) and determining the resulting % error of the NCPS (Net Count Per Second) based on the standard deviation σ value, given at 95% confidence level. Thus, Equation (3) is written as:

$$\sigma_n = \sqrt{\frac{r_{0Y}}{t_0} + \frac{r_{sY}}{t_s}} \tag{4}$$

where:

r_{0Y}, r_{sY} is the net count rate at the gamma line (Y) for background and the sample, t_0, t_s is the real counting time of the background and the sample respectively.

3. RESULTS AND DISCUSSION

3.1. Preliminary test

The preliminary analysis of the measured spectra was conducted by Genie2k software in combination with LabSOCS geometry model (counting efficiency). The radiochemical recovery was calculated by comparing ^{133}Ba photopeak area in the sample spectra with the ^{133}Ba photopeak area in the spectra of a standard source. The obtained results (Table 1) have shown that the values are in good agreement with the expected values independently if the 186 keV photopeak of ^{226}Ra (samples DG1, DG2 and DG3) or if the photopeaks of its daughters ^{214}Pb and ^{214}Bi were used for activity concentration calculations (sample DG3 only). The preliminary test confirmed that ^{226}Ra can be detected and its content accurately determined in a water sample by the herein described method.

Table 1. Results obtained by preliminary tests. Uncertainty is given at k =2.

Samples	Radio-chemical recovery	Calculated activity [Bq/kg]	Reference activity [Bq/kg]
DG1	1.00 ± 0.05	0.37 ± 0.08	0.37 ± 0.04
DG2	0.96 ± 0.04	0.23 ± 0.06	0.25 ± 0.04
DG3	1.00 ± 0.05	0.16 ± 0.08	0.14 ± 0.02

3.2. Validation of the radiochemical method

In order to further validate the method, two “control” samples were analyzed. The samples were measured 3 days after the source preparation and the measured spectra were at this stage analyzed in two different ways. The LabSOCS geometry modeling was used to simulate detector efficiency curve (results are labeled “LabSOCS” in the tables). The samples are spiked with a known amount of ^{226}Ra and ^{228}Ra standard solutions. ^{133}Ba was used as a radiochemical recovery tracer. The gamma sources were re-measured after 20 days, which allowed for radioactive equilibrium between ^{226}Ra and its daughters ^{214}Pb and ^{214}Bi to be established. The counting efficiency for ^{214}Pb and ^{214}Bi was calculated by using LabSOCS software (results are labeled “LabSOCS – via daughters” in the tables) in order to calculate ^{226}Ra activity concentrations in the samples. The tables 2 and 3 summarize the ^{226}Ra and ^{228}Ra results and their radiochemical recoveries. The results show that ^{226}Ra activity concentrations determined by the use of the herein described method in combination with LabSOCS software are in agreement with the reference values. The ^{228}Ra activity concentrations determined by the herein described method in combination with LabSOCS software are all in agreement with the expected values.

Table 2. Results of the ^{226}Ra analysis. Uncertainty is given at k =2.

Samples by methods	Radio-chemical recovery	Calculated activity [Bq/kg]	Reference activity [Bq/kg]
LabSOCS - (GS1)	1.00 ± 0.06	0.44 ± 0.08	0.44 ± 0.04
LabSOCS - (GS2)	0.93 ± 0.04	0.75 ± 0.12	0.82 ± 0.06
LabSOCS via daughters - (GS1)	1.00 ± 0.06	0.42 ± 0.06	0.44 ± 0.04
LabSOCS via daughters - (GS2)	0.93 ± 0.04	0.73 ± 0.10	0.82 ± 0.06

Table 3. Results of the ^{228}Ra analysis. Uncertainty is given at k =2.

Samples by methods	Radio-chemical recovery	Calculated activity [Bq/kg]	Reference activity [Bq/kg]
LabSOCS - (GS1)	1.00 ± 0.06	0.40 ± 0.04	0.37 ± 0.04
LabSOCS - (GS2)	0.93 ± 0.04	0.69 ± 0.04	0.68 ± 0.06

The calculation of Minimum Detectable Activity (MDA) for a given nuclide, at the 95% confidence level, is done according to Currie’s formula [5].

$$\mathrm{MDA(Bq/kg)}=(2.71+4.66(\sigma))/(T*EFF*Y*m) \tag{5}$$

where σ is the standard deviation of the background collected during time, T is the collect time (sec), EFF is the efficiency at the energy of interest, Y is Branching Ratio and m is sample mass.

For the herein described method (gamma spectrometric determination) the minimum detectable activities (MDAs) for 8L of sample and a measuring time of 2.3 days are:

- For direct determination of ^{226}Ra via its 186 kev gamma peak MDAs of 60-70 mBq/kg were calculated.
- For determination of ^{226}Ra via its daughters ^{214}Pb and ^{214}Bi MDAs of 6-8 mBq/kg.
- For determination of ^{228}Ra via its daughter ^{228}Ac MDAs of 16-20 mBq/kg.

4. CONCLUSION

This work is aimed to the validation of the methodology for the determination of ^{226}Ra and ^{228}Ra in environmental samples by γ-spectrometry. Micro-coprecipitation as barium (radium) sulfate was successfully modified to allow for direct determination of ^{226}Ra and ^{228}Ra by gamma spectrometry. However, large volumes of samples and/or long waiting time (20 days), before radioactive equilibrium is established, are required for accurate ^{226}Ra activity concentration determination. The reasons for the latter are the lower emission probabilities and counting efficiencies when compared to alpha-spectrometric determination. ^{228}Ra activity concentration determination by the herein described method on the other hand offers some important advantages when compared to, for example, standard radiochemical methods using chromatographic separations in combination with liquid scintillation counting technique. The most important advantages are: i) it is not necessary to separate ^{228}Ra (or its daughter ^{228}Ac) from other beta-emitting radionuclides before counting, thus allowing a simple and fast sample preparation, and ii) due to the fact that secular radioactive equilibrium between ^{228}Ra and its daughter ^{228}Ac is established in 30 hours, the waiting time between the source preparation and the start of the measurement is relatively short, thus enabling the analyst to obtain results in a reasonable time span. Overall best results were obtained when the herein described method was combined with LabSOCS calculations.

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