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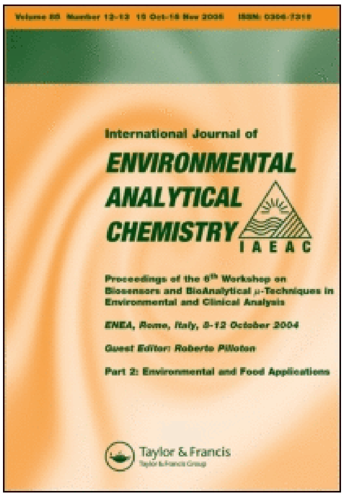

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IMPLEMENTATION OF A SEQUENTIAL INJECTION PRE-TREATMENT METHOD FOR SIMULTANEOUS RADIUM AND STRONTIUM DETERMINATION

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A semi-automatic procedure for the simultaneous determination of Ra and Sr in two steps has been developed. In the first step, separation and pre-concentration of both analytes is performed by using a sequential injection procedure. In the second step, the activities of ^{226}Ra and ^{90}Sr, alpha and beta emitters, respectively, are determined using a low background proportional counter at the corresponding plateau potentials. ^{226}Ra concentration is obtained by a single measurement of the precipitate. ^{90}Sr activity is determined by means of its daughter ^{90}Y carrying out two different measurements along the first day after the separation process; the solution of the Bateman radioactivity decay equations allows to obtain the initial ^{90}Sr–^{90}Y activities. The activities analysed in the present work have been ranged between 0–14 Bq/L for ^{226}Ra and 0–175 Bq/L for ^{90}Sr.

Keywords: Radium-226; Strontium-90; Simultaneous determination; Sequential injection

INTRODUCTION

^{226}Ra and ^{90}Sr, primordial and anthropogenic isotopes, respectively, can be found together in some environmental samples. ^{90}Sr is a fission product that has been released into the atmosphere as a consequence of the nuclear tests carried out since 1945. This isotope, after deposition on the soil by means of rain [1,2], can be filtered into the soil and be found in some mineral waters, in which the Ra concentration is usually high [3–5].

Both isotopes are among the major contributors to the overall collective dose due to their long half-life [6,7]. On the other hand, since the former chemical elements are analogues of calcium, they can be incorporated into the trophic chain and

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settled preferentially in bones of humans and other vertebrate organisms. Consequently, the search for methods to determine both isotopes can be considered of great importance in the environmental field.

^{226}Ra determination requires both the co-precipitation with a stable carrier and its separation from other possible interferents, which also could produce α-emission or an increase in the precipitate thickness with the corresponding self-absorption effect. For the β-emitter similar requirements to the above-mentioned are needed, although the self-attenuation is lower than that for α-emitters. The simultaneous determination of ^{226}Ra and ^{90}Sr should take into account these aspects, the obtained precipitate being of low thickness.

On the other hand, the sequential injection (SI) [8,9] allows one to carry out the analytical procedure automation with advantages over its parent (flow injection, FI). These mainly consist in: the manifold simplicity, the possibility of experimental parameter modification via software and a saving in reagent consumption. The previous aspects provide wider possibilities in the field of radiochemistry determinations. The importance of automation lies in the convenience of reducing the analysis times and improving the corresponding throughput. In this way, the sample handling by the analyst is minimised, which is important when the activity is high, and a considerable reduction in the reagent consumption and waste output are achieved.

Nevertheless, in spite of these clear advantages, the number of references that can be found in the literature on SI radiochemistry determinations is still scarce [10–18]. Recently some critical reviews on the topic of sequential injection analysis (SIA) [19], monitoring of environmental parameters by SIA [20] and automated analytical separations in radiochemistry have been published [21].

In this work we have developed a semi-automatic SI procedure for the simultaneous determination of ^{226}Ra and ^{90}Sr. The separation process is carried out by the adsorption of the two elements, or their daughters, onto a MnO_2-impregnated cotton filter. The basis for the individual isolation method has been described elsewhere [15,16]. However, several modifications were needed to implement the simultaneous determination in the semi-automatic system. The concentration of the ^{90}Sr isotope has been determined from its daughter (^{90}Y), assuming that secular equilibrium between the former existed previously in the analysed sample. This option has been also used by other authors [22,23] and applied in the present work because Sr is very scarcely retained in the adsorption process under our working conditions.

After their elution with hydroxylamine, Ra and Y isotopes are sequentially co-precipitated with barium sulphate in a buffered acidic medium and with iron (III) hydroxide in an ammonia medium, respectively. Once the isotope isolation has been accomplished, their corresponding concentrations are determined by using a low-background α–β proportional counter. The main limitation for carrying out automatic measurements of the α or β emissions lies in the nonavailability of continuous commercial detectors for low activity levels, as usual in environmental samples. Up to date only fully automated procedures have been applied to samples with high ^{90}Sr activities coming from nuclear waste [10,14].

The recovery obtained for ^{226}Ra and ^{90}Y is high (80 and 90%, respectively) although a small fraction of ^{90}Sr ($\sim$20%) passes to the filtrate. The initial ^{90}Sr activity in the analysed sample is obtained by carrying out two β-determinations within a 24 h time interval and applying the Bateman equations.

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EXPERIMENTAL

Reagents

The following solutions, prepared with analytical grade reagents, were used:

0.1 M potassium permanganate,
0.1 M hydroxylamine (in a 0.2 M HCl medium),
2 M acetic acid–acetate buffer of pH 4.8 (containing 0.2 mg/mL of Ba^{2+}),
1 M sodium sulphate,
25% ammonia solution,
1 mg/mL iron (III) hydroxide.

Radium-226 and Sr-90/Y-90 solutions were obtained by dilution from standards, supplied by CIEMAT (Madrid, Spain), with concentrations of 36.2 ± 0.5 Bq/mL and 108.46 ± 0.2 Bq/g, respectively. Cotton filters were made with absorbent cotton wool used in health care. The Millipore filters used were of 0.22 and 0.45 μm porous size and 47 mm diameter.

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Apparatus and Software

The SI setup used in the method contains the following elements:

- A Personal Computer to control all other elements.
- A Crison Microbur 2031 autoburette acting as the propelling pump equipped with a 5 mL syringe.
- A Crison double valve module equipped with an eight port selection valve and a six port injection valve.
- A Crison Microsampler 2040 autosampler.

All connections were made from polytetrafluoroethylene (PTFE) tubing of 0.5 mm inside diameter (id) (except the hold up loop of 1.5 mm id and 4.0 m length). The cotton filter was in a methacrylate tube of 3.5 mm id and 3.5 cm length which was submerged in a thermostatic bath (70°C). The automatic system is similar to that designed and used by the authors for ^{226}Ra determination [15].

The instrumental control was performed by using the software package *AUTOANALYSIS*[1] v. 4.0 [24] developed by the authors' group. The program allows automatic implementation of sequential injection experiments by introducing such information as the operational sequence to be followed (valve motion, aspiration and injection from the burette, delay times, etc). While the sequence is being executed, the computer controls the entire instrumental setup and ensures that no valve motion takes place while the burette is working.

Radioactivity Determination

Total α and β-activities were determined by means of a Tennelec LB 1000 low background proportional counter. The counter was calibrated with ^{241}Am and ^{90}Sr–^{90}Y

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[1] The software used in this work can be obtained on request. E-mail: AEST@p01.uib.es

standards by using potentials of 1100 and 1600 V corresponding to the α and β-plateaus, respectively. The total yields obtained for the α and β-countings were 18 and 34%, respectively.

Procedure

The file which stores the operational sequence starts with a sentence commanding the cleaning of all tubes. A coil between the autoburette and the selection valve is used to carry out the following steps.

(a) Filling of all aspiration tubes to the selection valve with the corresponding reagents.
(b) Aspiration and expelling of 4 mL of 0.1 M potassium permanganate through the cartridge. Process is delayed for 1 min to produce the formation of MnO_2 precipitate on the cotton fibre. After this step, deionised water is passed to eliminate the excess of potassium permanganate.
(c) Sample aspiration and expelling through the cartridge to produce isotope adsorption on the manganese dioxide. The total volume to be passed will depend on the sample activity. In our case we worked with samples of a 40 mL volume.
(d) Expelling of hydroxylamine to elute the MnO_2 deposit and the adsorbed isotopes and further spilling to the autosampler vessel.
(e) Adding of 4 mL of acetic-acetate buffer containing 0.8 mg of Ba(II).
(f) Adding of 8 mL of sodium sulphate.

After the isotope elution, precipitation of $Ba(Ra)SO_4$ is accomplished in the sample set and the sulphate precipitate obtained is isolated using a 0.22 µm filter. Then, the filtrate solution is carried to pH 9 with ammonia and Y is co-precipitated with iron(III) hydroxide and separated using a 0.45 µm filter.

Finally, both precipitates are dried under an infrared lamp and their activities are measured by the proportional counter at the corresponding potentials.

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RESULTS AND DISCUSSION

The working conditions have been optimised following an uniparametric method and taking into account the values obtained in single determinations.

Sample Volume and pH

The sample volume to be analysed will be conditioned by the isotope concentrations. We sized the volume to maintain an appropriate sampling rate. Obviously, if the isotope activities happened to be higher, the sample volume analysed could be reduced with the corresponding increase of the sampling frequency.

The sample pH which passes through the absorption column should not be acidic since the MnO_2 precipitate could then be solubilised and, thus, the sample has been neutralised with ammonia prior to isotope determination. We have checked that using several frequent buffers at this pH range (i.e., phosphate) the isotope recovery was lower.

Isotope Co-precipitation

In the literature, the single determinations of ^{226}Ra [25,26] or ^{90}Sr [27,28] by means of co-precipitation are usually carried out using $BaSO_4$ or $SrCO_3$, respectively, as the most common precipitants because of the high yields obtained in their radiochemistry separations. However, when we tried to use $BaSO_4$ to co-precipitate simultaneously both isotopes, the chemical yield for ^{90}Sr was lower. Moreover, in the simultaneous ^{226}Ra and ^{90}Sr determination, the use of $BaCO_3$ gave rise to poor results for ^{226}Ra. Due to these facts a mixture of the two co-precipitants was tested, but the resulting yield did not improve significantly. In consequence, we decided to determine ^{90}Sr from its daughter ^{90}Y. This option can be considered feasible since, with the selected working conditions for the adsorption process, Ra and Y are well retained, whereas only a small Sr fraction ($\sim 20\%$) is adsorbed. Therefore, once the eluted solution is obtained, Ra is co-precipitated with $BaSO_4$ at pH 4.8, which is provided by an acetic acid-acetate 2 M buffer. Then, filtration is carried out using a 0.22 µm filter. It has been checked that larger porous sizes do not retain all the obtained precipitate. The Ba (II) amount added in all cases has been of 8 mg in order to avoid self-absorption problems.

In the above-mentioned conditions, yttrium remains in the filtrate and the solution is carried to a basic medium of pH 9 with ammonia. Then, yttrium is co-precipitated with iron (III) hydroxide and separated with a 0.45 µm porous size filter. As a result, two precipitates were obtained and further dried under an infrared lamp.

Once the experimental conditions were determined, the recovery of the process was determined by means of the ^{226}Ra and ^{90}Sr standards described above. The mean recovery obtained was 80% for ^{226}Ra and 90% for ^{90}Sr.

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Activity Measurements

The activity measurement of each isotope is carried out by a different procedure due to the differences between the half-life of their corresponding daughters. Whereas for ^{226}Ra ($t_{1/2}$ of 1643 years) its first daughter is ^{222}Rn with a $t_{1/2}$ of 3.82 days, for ^{90}Sr ($t_{1/2}$ of 30.2 years) its daughter is ^{90}Y, with a $t_{1/2}$ of 64.1 h, which produces ^{90}Zr, a stable isotope.

As established in the single determination [15], the activity of ^{226}Ra can be obtained directly in less than 12 h after the isotope separation, in which its variation happens to be negligible. With respect to ^{90}Sr, determination of the activity from its daughter ^{90}Y has the advantage that it can be calculated from two measurements obtained in a 24 h period, the first just after drying the filter and the second the following day. To estimate the initial ^{90}Sr concentration in the analysed sample we assume the existence of an initial secular equilibrium respect to its daughter and, consequently, both activities should have the same value. Otherwise, if the initial ^{90}Sr activity was obtained directly, it would be required to wait until a week after the first activity measurement in order to reach the new secular equilibrium. The initial ^{90}Y concentration is calculated by means of the Bateman decay equations from the two β-countings obtained, which is shown below:

$$A_{Y90}(0) = A_T(t_1)e^{\lambda_B t_1} + \frac{A_T(t_2)e^{\lambda_B t_2} - A_T(t_1)e^{\lambda_B t_1}}{2(e^{\lambda_B t_2} - e^{\lambda_B t_1})}(1 - 2e^{\lambda_B t_1})$$

where $A_{Y90}(0)$ is the initial ^{90}Y activity ($t = 0$), λ_B is the ^{90}Y decay constant, $A_T(t_1)$ is the total β-activity at time t_1, $A_T(t_2)$ is the total β-activity at time t_2. To obtain this equation

TABLE I Results obtained in the analysis of ^{226}Ra and ^{90}Sr standard solutions by using a volume of 40 mL

	Added (Bq/L)		*Found* (Bq/L)*	
	^{226}Ra	^{90}Sr	^{226}Ra	^{90}Sr
Sample 1	7.0	31.9	5.8 ± 0.3	26.0 ± 1.7
Sample 2	7.0	116	6.9 ± 0.3	115 ± 5
Sample 3	9.2	116	9.5 ± 0.5	126 ± 5
Sample 4	13.9	174	15.2 ± 0.5	150 ± 12

*Mean ± *SD* ($n = 3$).

we have assumed that the values t_1 and t_2 are much lower than the ^{90}Sr half-life and consequently $\exp(-\lambda_A \cdot t_1) \approx \exp(-\lambda_A \cdot t_2) \approx 1$, where λ_A is the ^{90}Sr decay constant.

The method has been tested using spiked water samples with a wide range of activities for both isotopes. In spite of the fact that the activities considered are higher than both those expected for environmental samples and that of the EPA limit for ^{226}Ra (0.19 Bq/L) and ^{90}Sr (0.30 Bq/L) in drinking waters, these values can be found in contaminated samples or in hot spring waters for ^{226}Ra [5,26,29]. In addition the LLDs obtained for the method, 0.15 Bq/L for ^{226}Ra and 1.0 Bq/L for ^{90}Sr, support the fact that the method can be applied to some environmental samples.

Activities shown in Table I have been obtained by means of the Bateman equations for ^{90}Y assuming a secular equilibrium with its parent. These values have been corrected with the average recovery, which has been of 80% for ^{226}Ra and 90% for ^{90}Sr. Taking into account that the most frequent ions found in water do not interfere in the yield of the process [15,16], and that the results are in reasonable agreement with the added activities of both isotopes, the method proposed here could be applied to real polluted environmental samples.

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CONCLUSIONS

1. An implementation of a semi-automatic SI method for the simultaneous ^{226}Ra and ^{90}Sr pre-concentration and separation has been developed with the corresponding increase in the sampling rate with respect to the single methodologies.
2. The two isotopes are isolated by sequential co-precipitation in 20 min without any intervention of the analyst. ^{226}Ra activity is obtained from a single measurement of the alpha activity whereas for ^{90}Sr two measurements of the beta activity are needed in a time period of one day. This latter activity is calculated from its daughter ^{90}Y assuming an initial secular equilibrium between the two isotopes. Using this procedure, different standards have been analysed with satisfactory results.
3. Efforts to develop continuous measuring systems and the whole automation in the alpha and beta determinations (as in high as in low activity levels) should be undertaken.

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