Validation and implementation of a method for ^{226}Ra determination by using LSC

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Abstract

A co-precipitation method followed by a liquid-liquid extraction and liquid scintillation counting is validated by applying it to five different types of matrices. In order to test the applicability of the method, complex matrices are selected. This paper shows the implementation and the results of the validation of the method.

Keywords

^{226}Ra, activity, liquid scintillation counting, implementation, validation

Highlights

- A new LSC method to measure ^{226}Ra in different matrices that is useful when low detection limits are needed is validated.
- Validation tests accuracy, linearity, ruggedness, selectivity and sensitivity.
- The implementation of the method is shown.

1. Introduction

A method to measure ^{226}Ra in solid samples with very low detection limits has been developed by Idoeta et al. [1]. This paper also contains a revision of the methods usually used for ^{226}Ra determinations and an analysis of the advantages of the proposed method.

The developed method consists of the use of a High Pressure Asher to dissolve samples, and a Ba-Ra co-precipitation followed by a liquid-liquid extraction process. The Rn emanated from the obtained sample is measured using a liquid scintillation counter (LSC). This method is a combination of two other methods: a commonly used procedure to concentrate Ra [2] and a standard method for achieving low detection limits for water samples [3]. The comparison between the results obtained by applying a conventional Ra radiochemical separation method followed by alpha spectrometry measurement and the method described in the Idoeta et al. paper [1] shows that both provide comparable performances when low detection limits are needed. Detection

limits lower than 1 Bq/kg detection limit are achieved when measuring 1 g of test-sample for 3 h [1].

This paper presents the implementation and validation of this method.

Validation is carried out by using samples coming from different complex matrices, defining its complexity in view of the chemical and radiological interferences they provoke when ^{226}Ra is determined in them by using the developed method. Some of these matrices are mineral (soil, calcium carbonate and phosphogypsum) and others are organic (seaweed and milk).

The quality parameters tested in the validation procedure are precision, trueness, linearity, ruggedness, selectivity and sensitivity [4-6], together with values for detection limits, uncertainties and chemical recovery yields. Precision is tested in intra-laboratory conditions.

Method implementation has been done by means of the optimization of the parameter settings in the specific equipment (atomic absorption spectrometer and liquid scintillator counter) used in the laboratory when this method is applied.

2. Method implementation and validation

2.1. Materials and equipment

2.1.1. Samples

To accomplish method validation, five different matrices have been used, all of them being reference materials. They have been selected not only for their diversity, nature and activity concentration, but also because of their complexity. This complexity involves two different aspects, as explained in the previous reference paper of Idoeta et al [1]:

- Chemical interference that the composition of the samples could have on the radiochemical separation and its recovery (mainly because of the possible presence of Ca).
- Radiological interferences that could affect ^{226}Ra activity quantification (mainly in case of presence of ^{224}Ra).

Taking these factors into account, the samples selected were six reference materials coming from different interlaboratory comparison exercises (ILC); four of them organized by International Atomic Energy Agency (IAEA): soil (IAEA-CU-2010-04), seaweed (IAEA-446), phosphogypsum (IAEA-CU-2008-03) and calcium carbonate (IAEA-TEL-2017-04) and the last 2, milk and another soil, by the Spanish Nuclear Safety Council (CSN-CIEMAT).

2.1.2. Liquid scintillation spectrometer

An ultra-low background liquid scintillation spectrometer 1220 QUANTULUS^{TM}, from PerkinElmer is used.

This instrument is comprised of two low noise and background photomultiplier tubes. Sample detector assembly also includes light-emitting diodes and guard detectors. Its pulse shape analyser allows simultaneous alpha/beta discrimination counting and background for alpha emitters is less than 0.1 cpm [7].

The scintillation cocktail used is the water-immiscible Ultima Gold F (PerkinElmer), to allow only ^{222}Rn to get into the scintillation cocktail phase.

The sample counting is performed in the alpha/beta discrimination mode when secular equilibrium between ^{226}Ra and its daughters is achieved. Alpha emissions from ^{222}Rn (5.49 MeV) and its daughters, ^{218}Po (6.00 MeV) and ^{214}Po (7.69 MeV), are registered in the spectrum. These three emissions are all taken into account for ^{226}Ra activity concentration calculations; this way, the detection efficiency for alpha particles is around 280% out of a maximum of 300%. This efficiency is both detection and extraction efficiency. It is known [8] that the distribution of ^{222}Rn between the different phases in the vial depends on the chemical conditions of the liquids present in the vial, the temperature, and vial material. In our method, vial type, temperature, and chemicals added are always the same; only the Ba carrier could be different depending on the chemical recovery yield. The effect of the amount of Ba in the vial was studied in the previous work of Idoeta et al [1] and it was found that it does not interfere in the measurement by LSC.

Pulse shape analysis (PSA) is used for alpha/beta discrimination. Following the method described by Forte et al. [9], an optimum PSA setting of 100 has been established measuring the ^{226}Ra calibration source, prepared for its measurement in the same way as the samples, after reaching the isotopic equilibrium, at different PSA values (between 50 and 150). Obtained counts in the alpha window for each PSA are fitted to a 3rd polynomial curve and its inflection point is defined, which corresponds to the optimum PSA.

Calibration sources are prepared by taking aliquots of a ^{226}Ra certified reference material, provided by the CIEMAT (MRC2004-022).

2.1.3. Atomic absorption spectrometer

The chemical recovery yield for Ra is calculated by adding a known amount of Ba carrier to the test sample before its digestion and measuring it after Ra co-precipitation by atomic absorption (AA) spectrometry. The Ba carrier used comes from Alfa Aesar (barium chloride dehydrate, ACS).

Atomic absorption spectrometry is carried out in an Analyst 200 Atomic Absorption Spectrometer from PerkinElmer. It consists of a high efficiency burner system with a nebulizer and a double beam spectrometer based on flame atomic absorption, with an optical system that allows compensation for possible changes in the intensity of the lamp. It has a highly sensitive solid state detector that works with high

efficiency in the UV region. It is possible to measure difficult elements with excellent signal-to-noise ratios.

The light sources used are a hollow cathode lamp (HCLs) and electrode less discharge lamps (EDLs). Following the work conditions defined in its manual [10], the range of this spectrometer is from 0 ppm to 20 ppm, a range in which the calibration curve maintains its linearity. Working wavelength is 553.6 nm.

2.2. Methods

2.2.1. Sample preparation and measurement

As explained in Idoeta et al. [1], the proposed method consists of the following main steps:

First, solid samples are dissolved using conventional methods, such as high-pressure digestion. Ra is isolated from the samples, following the procedure proposed by the IAEA to determinate Ra in environmental liquids or digested samples [2].

After sample digestion, the Ra from the sample is co-precipitated with $BaSO_4$. Next, the solution containing Ra and Ba precipitates is dried in an oven and dissolved using EDTA 0.25 M and ammonia.

According to the ISO 13165-1 standard [3], 10 mL of the solution obtained in the previous step are added into a PTFE (Polytetrafluoroethylene) coated 20 mL polyethylene vial together with 10 mL of water-immiscible scintillation cocktail. An aliquot of 0.5 mL of the same solution is taken to determine the recovery through Ba atomic absorption spectrometry.

To allow secular equilibrium between ^{226}Ra and ^{222}Rn, vials are stored in the dark for at least 25 days, inside the scintillation chamber at a constant temperature of around 18 °C. The ^{222}Rn emanated from the sample enters the scintillation cocktail and its alpha emissions, together with those coming from ^{218}Po and ^{214}Po, are recorded in the alpha spectrum. Vials are not shaken; this fact, important for ^{222}Rn measurements by LSC, is not so for ^{226}Ra determinations, as previously demonstrated [1].

A blank sample is prepared with distilled water following the same procedure as for the sample. A calibration source is prepared by spiking a blank sample with ^{226}Ra certified reference material and is measured for 3 hours once the isotopic equilibrium between ^{226}Ra and ^{222}Rn is reached, 25 days after its preparation.

Finally, the ^{226}Ra activity concentration is calculated following Eq. (1):

$$A_{Ra} = \frac{r_g - r_0}{\varepsilon \cdot m \cdot R} \quad (1)$$

where A_{Ra} is ^{226}Ra sample's activity concentration, r_g is the gross count rate of ^{222}Rn+^{218}Po+^{214}Po and r_0 is that of the blank, m is test sample mass, R is the chemical recovery yield and ε is the detection efficiency. ε and R are calculated following Eq. (2) and Eq. (3), respectively:

$$\varepsilon = \frac{r_{Sg}}{A_S \cdot m_S} \quad (2)$$

$$R = \frac{Ba,m}{Ba,a + Ba,e} \quad (3)$$

where r_{Sg} is the calibration count rate, A_S is the activity concentration of the ^{226}Ra certified standard solution added to the calibration source and m_S its mass, *Ba,e* and *Ba,m* are the native Ba present in the sample and the amount of Ba measured after separation, respectively, both measured by AA spectrometry; *Ba,a* is the amount of Ba added to the sample.

2.2.2. Method implementation

The implementation of this method in the laboratory implies the proper selection, when possible, of the equipment parameters. For the equipment used in this work, this selection has been carried out as follows.

Liquid scintillation spectrometer

In order to optimise counter settings and to check the stability of 1220 Quantulus, the following tests are carried out:

1220 Performance test [7] is carried out quarterly. This test involves efficiency and background assessment, guard counter check and noise test. To do it, ^{3}H, ^{14}C and background unquenched standards are used.

Equipment stability is tested on a daily basis. This test is carried out by measuring a ^{3}H unquenched standard for 2 minutes, checking that its count rate is within the average count rate ± 2 %.

In addition, a test of the PSA discrimination parameter setting is conducted yearly to check the optimum PSA value.

The selected spectrometer provides very high efficiency for alpha counting and its background ranges from 0.05 to 0.1 cpm when PTFE coated 20 mL polyethylene vials are used, allowing for very low detection limits.

To obtain similar count rate uncertainties, test-samples were measured for times ranging from three to twenty-four hours, depending on their activity. The blank is also measured for twenty-four hours.

Atomic absorption (AA) spectrometer

When measuring Ba by AA one should account for the fact that Ba suffers from self-ionization in the flame. For that reason, 2000 ppm of KCl is added to the test sample for AA measurement, since K is more self-ionizing than Ba.

In addition, if Ca is present in the sample, it can contribute to spectral interference, since CaOH emits in the same wavelength as Ba. Hence, a nitric oxide/acetylene flame

is used, which also allows for the correction of the signal reduction generated by the presence of phosphates, silicates and Al in the sample.

To obtain the calibration curve, 3 standard solutions of 5, 10 and 20 ppm of Ba carrier are used. Once the calibration curve is obtained, a reference solution is measured as a quality control.

This calibration curve is determined before each batch of samples is measured.

2.2.3. Method validation

For method validation, uncertainty, detection limits and method chemical recovery should be determined together with accuracy (considering its two components: precision and trueness), linearity, sensitivity, selectivity, and ruggedness of the method [4-5, 11-12].

Considering ILC exercises, it should be pointed out that all samples described in section 2.2.1. belong to ILC in which our laboratory has participated. However, in all of them, ^{226}Ra activity concentration was determined by using different methods: the developed one and those commonly used by our laboratory that are within our accreditation scope (ENAC 350/LE560, according to ISO 17025 [13]). Thus, the aforementioned reference materials have been used to validate this developed method but the results that were sent to the ILC providers came from our accredited methods due to the requirements of the accreditation system to frequently participate in ILC's exercises.

Uncertainties, detection limits and decision thresholds.

Following the Guide to the expression of uncertainty in measurement (GUM) [14], the combined standard uncertainty of ^{226}Ra activity concentration, $u(A_{Ra})$, is calculated using Eq. (4) [1]:

$$u(A_{Ra}) = \sqrt{\left(\frac{r_g}{t} + \frac{r_0}{t_0}\right) \cdot \left(\frac{1}{\varepsilon \cdot m \cdot R}\right)^2 + [u_{rel}^2(\varepsilon) + u_{rel}^2(m) + u_{rel}^2(R)] \cdot A_{Ra}^{\,2}} \quad (4)$$

where $u(A_{Ra})$ is the uncertainty of Ra sample's activity concentration; t and t_0 are sample and blank counting time; $u_{rel}(\varepsilon)$ is the relative uncertainty of the detection efficiency; $u_{rel}(m)$ and $u_{rel}(R)$ are the mass and the chemical recovery relative uncertainties, respectively.

$u_{rel}(\varepsilon)$ includes the counting uncertainty of the calibration source and all the uncertainties related to the calibration source preparation: that of the activity concentration A_S from the calibration certificate, which has a value of 0.52%, and of the mass m_S added to the calibration source.

Detection limits, *DL*, are calculated in Idoeta et al. [1] following ISO standard 11929 [15] as:

$$DL = \frac{2 \cdot DT + \frac{k^2}{t \cdot \varepsilon \cdot m \cdot R}}{1 - k^2 \cdot [u_{rel}^2(\varepsilon) + u_{rel}^2(m) + u_{rel}^2(R)]} \quad (5)$$

where *DT* is the decision threshold:

$$DT = \frac{k}{\varepsilon \cdot m \cdot R} \cdot \sqrt{r_0 \cdot \left(\frac{1}{t} + \frac{1}{t_0}\right)} \quad (6)$$

k is the quantile of the standard normal distribution probability that takes a value of 1.65 for a confidence level of 95 % and where $k = k_\alpha = k_\beta$ making the probability of obtaining false positives and false negatives equal.

Precision

The precision of the method has been established under intra-laboratory conditions. 9 test samples of the same soil from certified material have been prepared. Each test sample, with the same mass, has been measured during a 3 h counting time.

The precision of this method has been estimated according to ISO 5725 [16].

The repeatability limit (r) is defined as:

$$r = K\sqrt{2\sigma^2} \quad (7)$$

where σ is the standard deviation of the mean value and *K* the coverage factor, which takes a value of 1.96 to provide an estimate of the range where 95% of the individual results should be.

Considering that the absolute bias (δ) between the activity concentration mean value, $\bar{A}_{Ra}$, and the reference activity, A_{ref}, is:

$$\delta = \left|\bar{A}_{Ra} - A_{ref}\right| \quad (8)$$

the acceptance criterion for precision is:

$$\delta \leq r \quad (9)$$

Trueness

The trueness of the method has also been obtained under intra-laboratory conditions using the results from the previous 9 soil samples, but also taking into account the results obtained from the samples from the other matrices analysed by the proposed method.

The trueness of a method has been evaluated through two parameters. The first one is the relative bias (δ_r), that is widely used but with its use part of the information is missing, specifically that contained in the measurement uncertainty and in the uncertainty of the reference value. This is why another parameter, ζ score, typically used in the evaluation of the interlaboratory comparison exercises [17], has also been used here. ζ score is calculated as follows:

$$\zeta = \frac{|A_{Ra} - A_{ref}|}{\sqrt{u(A_{Ra})^2 + u(A_{ref})^2}} \quad (10)$$

where $u(A_{Ra})$ and $u(A_{ref})$ are the combined standard uncertainties of the calculated activity and the reference activity concentration values, respectively.

The acceptance criterion for δ_r, considering not only the objectives of this work but also the typical uncertainties related to environmental measurements, has been considered to be below 20%.

The acceptance criterion for ζ scores is the following: ζ score should be lower or equal to 2, which means that only about 5% of scores should fall outside the range 0-2.

Linearity

The method linearity in a range refers not only to the fact that the method works properly in a wide range of activity concentration values, but also to the fact that the counting efficiency is independent of the activity and, therefore, a calibration curve is not needed in this range.

The samples chosen for this validation plan have activity concentration values between 17 and 19000 Bq/kg and then, the linearity of the method could be shown in this range.

To demonstrate this linearity, the reference values have been plotted against the experimental values, and the linearity of the adjustment controlled by means of a R^2 test.

Ruggedness

Ruggedness can be used as a criterion to determine if a specific method can be applied to different types of samples [18]. To check the ruggedness of the developed method, the obtained values of trueness and chemical recovery yields are analysed for the different matrices used for this validation plan.

Selectivity

This method is selective, since radionuclides dissolved in the final solution are in ionic form and cannot be absorbed into the scintillation organic cocktail phase [9], as

only gaseous materials can be trapped in the cocktail [18]. The selectivity of this method was analysed in the previous work by Idoeta et al. [1]. In that paper, those interferences that could affect the method, which can have a chemical and/or radiological origin, are studied.

Sensitivity

To rank the relative contribution of each parameter to total uncertainty (see Eq. (4)), a sensitivity analysis has been performed. This sensitivity analysis uses the variance partitioning analytical approach [6, 19] and thus, the *S(x)* relative contribution of a variable *x* to the total uncertainty is calculated by the fraction of the terms associated with its variance:

$$S(x) = \frac{\left(\frac{\partial A_{Ra}(r_g - r_0, m, \varepsilon, R)}{\partial x}\right)^2 \cdot {u_x}^2}{u(A_{Ra})^2} \quad (11)$$

In this Eq. (11), u_x is the standard uncertainty of a variable *x* and $u(A_{Ra})$ is the combined standard uncertainty of ^{226}Ra activity.

This sensitivity analysis shows which of these parameters contributes most to the method's uncertainty, depending on its value ranging from 0 to 1: net count rate, test sample mass, detector efficiency or recovery. This sensitivity analysis has been carried out for all samples measured.

3. Results and discussion

3.1. Uncertainties, detection limits and recoveries.

Table 1 shows the activity concentration obtained for all the analysed samples, A_{Ra}, with their combined standard uncertainty $u(A_{Ra})$, detection limit (*DL*) and chemical recovery yield. For sample soil-1, the values shown are the mean values from the 9 samples analysed; single values are shown in Table 2.

Table 1 Experimental A_{Ra} activity concentration obtained for the five analysed matrices with their combined standard uncertainties, $u(A_{Ra})$, detection limits, *DL*, chemical recovery yield, R

	A_{Ra} [Bq/kg]	$U(A_{Ra})$ [Bq/kg]	$U(A_{Ra})$ [%]	*DL* [Bq/kg]	*R* [%]
Seaweed	16.6	0.6	3.6	1.8	76.3
Phosphogypsum	818	31	3.8	3.1	78.7

Milk	16.6	0.7	4.4	0.2	68.3
Soil-1	17944	597	3.3	1	81.8
Soil-2	30.6	2.6	8.4	3.9	71.3
Calcium Carbonate	6972	181	2.6	2	70.9

As can be observed in Table 1, for activity concentrations ranging between 19000 Bq/kg and 17 Bq/kg, relative standard uncertainties are lower than 10% and detection limits are lower than 4 Bq/kg. These values demonstrate that this is quite a practical and stable method able to measure ^{226}Ra even when it is present in very low amounts.

Regarding recovery values, they are typically higher than 70%. It is only for milk samples that it is slightly lower.

3.2.Precision

As mentioned above, the precision of the method has been established preparing 9 test samples of soil and measuring them during 3h counting time. Table 2 shows the measured activity concentration values with their combined standard uncertainties, detection limits and chemical recovery yields. For these samples, the activity concentration reference value (A_{ref}) is 19050 Bq/kg and its uncertainty ($u(A_{ref})$) takes a value of 260 Bq/kg.

Table 2 Activity concentration, combined standard uncertainty, detection limit and recovery values for 9 soil sample aliquots, together with their mean value, standard deviation, S, and absolute bias, δ, from reference value.

	A_{Ra} [Bq/kg]	$U(A_{Ra})$ [Bq/kg]	*DL* [Bq/kg]	R [%]
1	18790	660.5	0.9213	85.38
2	18940	619.5	0.9568	82.45
3	18580	462.45	0.9455	83.02
4	18750	542	0.9731	80.26
5	18340	557.5	0.9172	82.74
6	17640	741	0.9495	81.78
7	18560	828.5	1.009	76.02
8	16310	459.95	0.8463	91.38
9	15590	497.85	1.054	73.21
Mean	17944	597	0.95	81.8
S	1204			
δ	1106			

δ, absolute bias, is obtained using Eq. (8), and it takes a value of 1106 Bq/kg. This value is lower than the repeatability limit, *r*, obtained by Eq. (7) of 1124 Bq/kg. Thus, the method is reliable with respect to precision [16].

This repeatability limit is comparable, as expected, to the uncertainties that would be obtained if k = 1.96 were selected and, thus, a confidence level of 95% is admitted.

3.3. Trueness

Table 3 shows, for each analysed sample, the activity concentration measured and its combined standard uncertainty, as well as the reference values. In order to evaluate the trueness of these values, relative bias and ζ are calculated and their values are included in Table 3 for evaluation.

Table 3 Experimental and reference activity concentration values (A_{Ra} and A_{ref}) with their combined standard uncertainties ($u(A_{Ra})$ and $u(A_{ref})$). Relative bias (δ_r) and ζ-score values are also included

	A_{Ref} [Bq/kg]	$U(A_{Ref})$ [Bq/kg]	A_{Ra} [Bq/kg]	$U(A_{Ra})$ [Bq/kg]	δ_r [%]	ζ
Seaweed	17.0	0.8	16.6	0.6	2.12	0.36
Phosphogypsum	780	62	818	31	4.86	0.55
Milk	16.3	0.8	16.6	0.7	1.96	0.30
Soil-1	19050	260	17944	597	5.80	1.70
Soil-2	32.9	1.9	30.6	2.6	6.99	0.72
Calcium Carbonate	6970	200	6972	181	0.03	0.01

For all matrices, the relative bias is much lower than 20% and ζ is lower than 2; therefore, there is no significant difference between the measured results and the reference values. Hence, the method is reliable with respect to trueness.

3.4. Linearity

Figure 1 shows the plot of experimental activity concentration versus reference activity concentration. Figure 1 also presents the goodness of the linear fit, which is 1.00, and the correlation equation: y = 0.95×x.

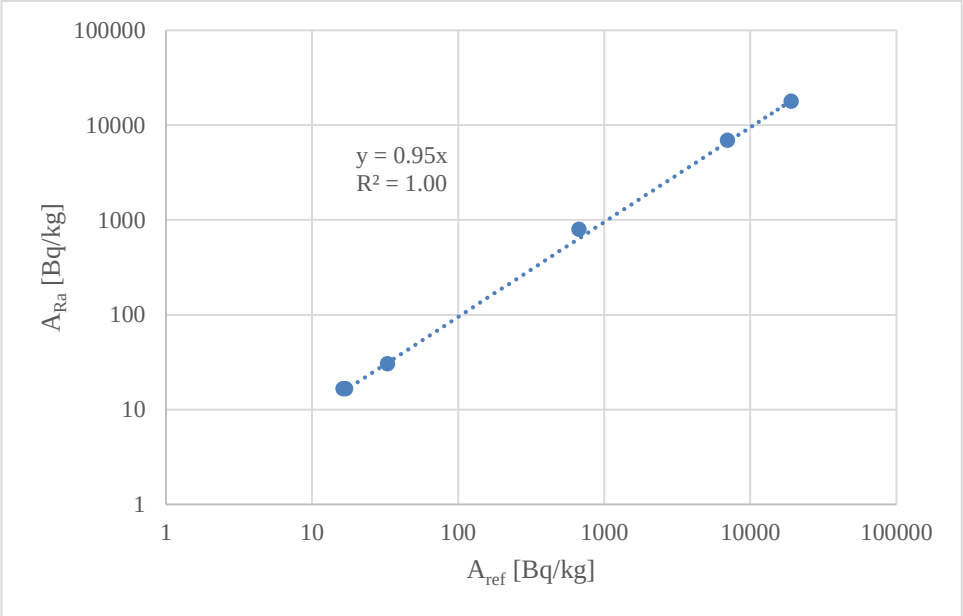

Figure 1 Measured activity concentration vs reference activity concentration, in [Bq/kg]

This result confirms the very good linearity of the method in the range measured [17 – 19000 Bq/kg]. In fact, a much broader range linearity of the method is expected, from the detection limit up to the case of very high activities where dead time becomes very relevant and dead time corrections are necessary.

3.5. Ruggedness

Looking at the obtained values of trueness (relative bias and ζ score) and recovery, shown in Tables 1, 2 and 3, it can be concluded that those values are not dependent on the matrix analysed nor on the level of activity concentration.

Regarding radiochemical yield, R, we can observe a tendency that links high Ca concentration with low recovery yields. Nevertheless, the relative standard deviation of R values in Table 1 is 7.8%, which is very similar to the 6.4% obtained in Table 2, being aliquots of the same sample. Regarding ζ scores, they are similar for all types of samples.

Regarding relative bias, δ_r, no tendency is found. Both soils present the largest δ_r, but the results shown in Table 2 show even a value of -0.6%. All relative bias found are much lower than admitted value of 20%.

Thus, the ruggedness of this method is well proven.

3.6. Selectivity

The selectivity of this method was analysed in Idoeta et al. [1], which analysed chemical and radiological interferences that could affect the method.

Results show that, among the different chemical components that samples could contain, only Ca and Sr were not effectively removed from the sample during co-

precipitation. Therefore, the presence of these elements and their impact on sample stability, radon transfer to the scintillation cocktail and the Ba concentration determination by AA, were studied. It was concluded that both chemical elements do not interfere when determining Ba by AA nor when performing the LSC measurement; only in the case where Ca content is close to the saturation level of the AA instrument could its presence be significant [1].

Regarding radiological interference, only the presence of ^{220}Rn precursors, especially ^{224}Ra, must be taken into account. However, this situation would be considered by the detection of ^{220}Rn progeny; if they appear, a new measurement should be done after a few days [1].

3.7. Sensitivity

Table 4 shows the *S(x)* relative contribution [%] of the analysed parameters (test sample mass (*m*), net count rate, detector efficiency (ε) and recovery (*R*)) to the activity uncertainty.

Table 4 S(x) relative contribution to activity uncertainty [%]

	S(m)	S(net count rate)	S(ε)	S (R)
Seaweed	0.007	76.63	17.83	5.53
Phosphogypsum	0.006	5.09	26.19	68.71
Milk	0.001	47.52	11.52	40.96
Soil-1	0.009	0.36	38.79	60.84
Soil-2	0.003	81.94	3.28	14.78
Calcium Carbonate	0.013	1.48	31.22	67.28

As expected, it can be observed that the contribution of mass to the activity concentration uncertainty is negligible. In the case of soil-1, phosphogypsum and calcium carbonate – those that have high activity – the variable that contributes most to uncertainty is that associated to the chemical recovery. In the case of seaweed, milk and soil-2, whose activity concentrations are much lower, the contribution of the counting statistics is the most important.

This sensitivity analysis shows that the method is especially sensitive to the chemical recovery and to counting statistics and, secondly, to the detection efficiency, but not to the weighing of the test sample.

To conclude the validation process, the results obtained for all this validation parameters are compared with other published validations results from methods employing LSC measuring technique for non-aqueous samples is not easy as available data are scarce. A similar method to ours can be found in reference [18] but the pre-treatment step and the tracer used are different. Detection limits found through this other method are similar as well as radiochemical yields, relative bias and ruggedness, but they applied only to NORM materials. Comparison to another method applied to

sediments that differs in the pre-treatment step, radiochemical yield measurement technique and in the fact that it does not use the liquid–liquid extraction step [20] shows that this method achieved lower radiochemical yields (mean value of 46%) than our method and worse relative biases when compared to the reference values.

Therefore, we can conclude that the goal of validation of this method, that is, to prove that it can be applied as a ^{226}Ra analytical method for different types of matrices, giving reliable and accurate results of analysis, is accomplished.

4. Conclusions

In this work, the co-precipitation method of determining radium has been adapted and validated for use with a liquid scintillation counter. The practical steps necessary to carry out the measurements suitably using the two particular kind of spectrometer needed in the performance of the method under quality assurance conditions have been detailed and the validity of this new method has been tested and found to be satisfactory. This method has been successfully implemented in our radiological environmental monitoring laboratory as a routine method for ^{226}Ra analysis in environmental real samples.

Results obtained in the validation of the LSC method for ^{226}Ra using five kind of reference materials show that they meet the previously defined requirements so that it can be considered as an accurate and reliable method to be used for a wide range of different sample matrices, independently of their nature and their activity concentration, and that it allows for the obtention of very low detection limits. The good agreement obtained between the results of this work and the reference values of the individual reference materials proves the successful implementation of the method.

For activity concentration values ranging between 19000 Bq/kg and 17 Bq/kg, relative standard uncertainties are lower than 10 % and detection limits are lower than 4 Bq/kg and are comparable to other methods, like alpha spectrometry, which is more expensive and time consuming. Chemical recovery values for Ra are typically higher than 70%.

Considering values of absolute bias and repeatability limit, this method is reliable with respect to repeatability when 9 aliquots of the same sample have been measured and compared with the reference value.

For all matrices, considering the relative bias and ζ values, it can be concluded that there is no significant difference between the measured result and the reference value and therefore, the method is reliable with respect to trueness.

Linearity is well probed by obtaining an $R^2 = 1$ in a linear adjustment between reference and measured activity concentration in the range studied.

The ruggedness of this method is demonstrated by obtaining similar values of trueness and recovery for different matrices and activity concentration levels.

The selectivity analysis has been performed in a previous paper with positive conclusions. Finally, it can be said that the method is especially sensitive to chemical recovery and counting statistics in case of low activity concentrations of ^{226}Ra.

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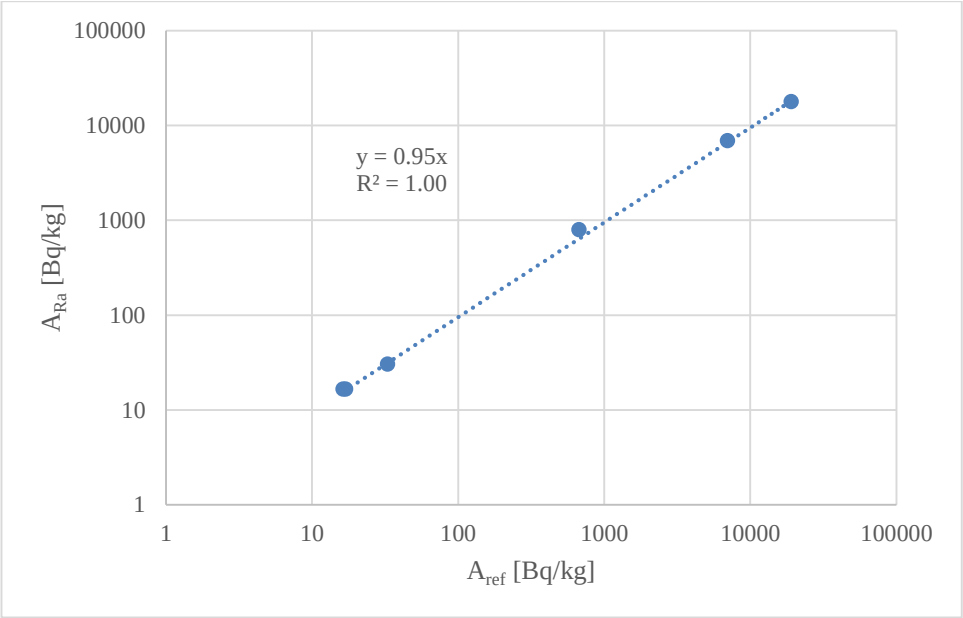

Figure 1 Measured activity concentration vs reference activity concentration, in [Bq/kg]

Table 1 Experimental A_{Ra} activity concentration obtained for the five analysed matrices with their combined standard uncertainties, $u(A_{Ra})$, detection limits, *DL*, chemical recovery yield, R

	A_{Ra} [Bq/kg]	$u(A_{Ra})$ [Bq/kg]	$u(A_{Ra})$ [%]	*DL* [Bq/kg]	*R* [%]
Seaweed	16.6	0.6	3.6	1.8	76.3
Phosphogypsum	818	31	3.8	3.1	78.7
Milk	16.6	0.7	4.4	0.2	68.3
Soil-1	17944	597	3.3	1	81.8
Soil-2	30.6	2.6	8.4	3.9	71.3
Calcium carbonate	6972	181	2.6	2	70.9

Table 2 Activity concentration, combined standard uncertainty, detection limit and recovery values for 9 soil sample aliquots, together with their mean value. Also included are the sample reference values: activity concentration and combined standard uncertainty

	A_{Ra} [Bq/kg]	$u(A_{Ra})$ [Bq/kg]	*DL* [Bq/kg]	R [%]	A_{ref} [Bq/kg]	$u(A_{ref})$ [Bq/kg]
1	18790	660.5	0.9213	85.38	19050	260
2	18940	619.5	0.9568	82.45		
3	18580	462.45	0.9455	83.02		
4	18750	542	0.9731	80.26		
5	18340	557.5	0.9172	82.74		
6	17640	741	0.9495	81.78		
7	18560	828.5	1.009	76.02		
8	16310	459.95	0.8463	91.38		
9	15590	497.85	1.054	73.21		
Mean	17944	597	0.95	81.8		
σ_r	1204					
δ	1106					

Table 3 Experimental and reference activity concentration values (A_{Ra} and A_{ref}) with their combined standard uncertainties ($u(A_{Ra})$ and $u(A_{ref})$). Relative bias (δ_r) and ζ-score values are also included

	A_{ref} [Bq/kg]	$u(A_{ref})$ [Bq/kg]	A_{Ra} [Bq/kg]	$u(A_{Ra})$ [Bq/kg]	δ_r [%]	ζ
Seaweed	17.0	0.8	16.6	0.6	2.12	0.36
Phosphogypsum	780	62	818	31	4.86	0.55
Milk	16.3	0.8	16.6	0.7	1.96	0.30
Soil-1	19050	260	17944	597	5.80	1.70
Soil-2	32.9	1.9	30.6	2.6	6.99	0.72
Calcium carbonate	6970	200	6972	181	0.03	0.01

Table 4 S(x) relative contribution to activity uncertainty [%]

	S(m)	S (net count rate)	S(ε)	S (R)
Seaweed	0.007	76.63	17.83	5.53
Phosphogypsum	0.006	5.09	26.19	68.71
Milk	0.001	47.52	11.52	40.96
Soil-1	0.009	0.36	38.79	60.84
Soil-2	0.003	81.94	3.28	14.78
Calcium Carbonate	0.013	1.48	31.22	67.28