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Determination of scaling factors to estimate the radionuclide inventory of wastes from the IEA-R1 research reactor

M. H. T. Taddei · J. F. Macacini · R. Vicente · J. T. Marumo · L. A. A. Terremoto

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Abstract Regulations for transfer and final disposal of radioactive waste require that the inventory of radionuclides for each package enclosing such waste must be estimated and declared. In this work, the scaling factor methodology was applied successfully to estimate the inventory of radionuclides in spent ion-exchange resins and spent activated charcoal, both with low and intermediate-activity level, from the IEA-R1 nuclear research reactor. Scaling factors or correlation functions were obtained linking the activity concentrations of 15 difficult to measure nuclides with two gamma-rays emitting key nuclides, reducing exposure to ionizing radiation, contamination risks and operational costs.

Keywords Research reactors · Radioactive waste assay · Difficult to measure nuclides · Scaling factor methodology

Introduction

The safety analysis of radioactive waste repositories is based on a set of critical radionuclides for which the combination of activity, half-life, mobility in the environment and radiotoxicity results in the highest radiological relevance for long-term disposal. Many of these relevant radionuclides cannot be measured directly by non-destructive methods in radioactive waste packages and are therefore generically designated as difficult to measure nuclides (DTMs) [1]. These radionuclides present at least one of the following characteristics: (a) emit no photons (gamma-rays or X-rays) at all; (b) emit photons with low energy and/or low absolute emission intensity; (c) have very low activity among the radioactive waste.

In most cases, the determination of the activity concentration of each DTM requires radiochemical analyses of radioactive waste samples in which the separation of the element from the waste sample matrix is necessary to allow detecting the radiations emitted and to ensure that the intended radionuclide is been measured. This separation is always complex and expensive [2]. Besides, sampling of these wastes may cause high radiation exposure to operators. As a consequence, if the number of packages to be characterized is large and many radionuclides are to be determined, cost and radiation exposure reasons require an alternative method for inventorying the radionuclide content of such wastes.

A currently accepted alternative methodology is the indirect determination of DTMs by scaling factors (SFs) or correlation functions (CFs), in which the activity concentration of each DTM is calculated multiplying the activity concentration of a key nuclide (KN) by appropriate factors obtained previously [1, 3, 4]. The SFs and CFs are specific for each nuclear facility, operational regime, radioactive waste stream and pair of DTM/KN nuclides. According to this methodology, empirical determinations of SFs or CFs obtained from a single set of representative radioactive waste samples are considered valid if the activity concentrations of each DTM obtained by direct radiochemical measurement and by use of SF or CF agree within a factor equal to or smaller than 10 [1, 3].

M. H. T. Taddei · J. F. Macacini
Laboratório de Poços de Caldas (LAPOC/CNEN-MG), Rodovia Poços de Caldas – Andradas Km 13, Poços de Caldas, MG CEP 37701-970, Brazil

R. Vicente · J. T. Marumo · L. A. A. Terremoto (✉)
Instituto de Pesquisas Energéticas e Nucleares (IPEN/CNEN-SP), Cidade Universitária, Avenida Professor Lineu Prestes 2242, São Paulo, SP CEP 05508-000, Brazil
e-mail: laaterre@ipen.br

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This work analyzed two batches of stored radioactive waste streams from the IEA-R1 nuclear research reactor, in order to obtain the SFs and CFs for each relevant DTM present. No previous comprehensive research concerning the inventory of radionuclides was performed on such radioactive waste streams.

The report of the inventory of radioactive waste packages is a regulatory requirement [5] and the SFs and CFs obtained will also be used in the characterization of the next batches of radioactive waste streams from this reactor.

Radioanalytical procedures adapted or developed in this work became the foundations for the characterization program of other radioactive waste streams from the IEA-R1 nuclear research reactor. Some of these procedures have been published recently [6–8].

In the scope of this work, the determination of the SFs and CFs followed the IAEA guidance [1] and the ISO standard method [9] on use of SFs for characterization of radioactive waste from nuclear power reactors.

The IEA-R1 is a 5 MW pool-type nuclear research reactor, moderated and cooled by light water, which achieved its first criticality in 1957. Located at the Nuclear and Energy Research Institute (IPEN/CNEN-SP), this reactor is still currently in use for scientific research and production of radioisotopes [10–12].

The cooling water of the IEA-R1 nuclear research reactor contains radionuclides originated in the reactor core and proceeding from activation of structural materials, irradiation of U compounds that are present as contaminants at very low concentrations on the external surface of the nuclear fuel cladding and, far more rarely, leakages that occur through discontinuities in the nuclear fuel cladding (situation which configures fuel failure).

In order to keep the overall concentration of soluble impurities around 2 ppm in the reactor pool water, there is a reactor's cooling water polishing system that consists sequentially of polypropylene filters, two activated charcoal beds and two mixed ion-exchange resins beds (cationic and anionic, with a volume of 0.5 m^3 each).

If the electrical conductivity of the reactor pool water turns to be outside the specified limits, the regeneration of the ion-exchange resins is performed and, when this regeneration does not work anymore, the replacement of filters, activated charcoal and ion-exchange resins is carried out.

Thereafter, the spent filters, activated charcoal and ion-exchange resins removed definitively from the reactor's cooling water polishing system become radioactive wastes with low- and intermediate activity level. Spent activated charcoal and spent ion-exchange resins concentrate most of the activity of these radioactive wastes.

As yet, only two batches of spent activated charcoal and of spent ion-exchange resins, that are presently stored and waiting treatment, were generated in two campaigns of replacement of the water polishing media in 1993 and 2003. All drums containing these wastes are equal and each of them has a volume of 200 L. As a whole, 14 drums contain a water suspension of granulated spent activated charcoal, whereas 7 drums contain a water suspension of spent ion-exchange resins, both with varying ratios of water-to-sorbent mass [13].

Before any treatment, the radionuclide content of each drum had to be determined individually so that it could meet the requirements of the regulatory authority for radioactive waste transfer and final disposal. All drums had to be characterized individually because, besides different radionuclide content, changes of operational regime, nuclear fuel chemistry or enrichment and rated power of the reactor usually have impacts on the activity of the radioactive wastes generated in different times.

Experimental

Sampling of radioactive wastes

A total of 42 samples were taken from drums containing spent activated charcoal and a total of 36 samples were taken from drums containing spent ion-exchange resins. Sampling of these wastes and preparation of the corresponding samples for the ensuing radioanalytical procedures were carried out following technical and safety standards [13].

Multiple samples were taken from some drums in order to test the homogeneity of the radioactive waste when different phases were visible within it. Activity concentrations of gamma-ray emitters (^{60}Co and ^{137}Cs) were measured in samples from different points of these drums. The deviation of these activity concentration measurements were mostly lower than 30 % [13], which indicates that the radioactive wastes can be considered homogeneous inside each drum [14].

Selection of radionuclides for measurements

Critical radionuclides usually cited [1, 3] in regulations concerning management of radioactive waste from nuclear power reactors were used as a reference set for this work. Results of the research carried out recently on radioactive wastes with low- and intermediate-activity level from the Brazilian nuclear power reactors [15–17] were also taken into account in the definition of the critical radionuclides set. Thereafter, those radionuclides (both KN and DTM), expected to be present in relevant concentrations among radioactive wastes with low and intermediate-activity level from the IEA-R1 nuclear research reactor [6–8, 13], were

selected for the radioanalytical procedures of the characterization program [13].

The chosen radionuclide set included activation products generated by irradiation of structural materials in the reactor core, along with fission products and isotopes of actinoid elements that have been generated by irradiation of the slight surface contamination of nuclear fuel assemblies or, far more rarely in the case of the IEA-R1 nuclear research reactor, that escaped from the irradiated nuclear fuel assemblies through discontinuities in its Al cladding.

Radionuclides selected for research were [13]: ^{3}H, ^{14}C, ^{55}Fe, ^{60}Co, ^{59}Ni, ^{63}Ni, ^{90}Sr, ^{99}Tc, ^{108m}Ag, ^{129}I, ^{135}Cs, ^{137}Cs, ^{234}U, ^{235}U, ^{236}U, ^{238}U, ^{237}Np, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu, ^{241}Am, ^{243}Am, ^{243}Cm and ^{244}Cm.

From this list of radionuclides, only ^{60}Co and ^{137}Cs were considered KNs because both are easily detected by gamma-ray scanning of the waste drums, whereas all other radionuclides in this set were designated as DTMs [13].

Procedures for analysis of key nuclides (KNs)

Each sample was analyzed for ^{60}Co and ^{137}Cs by gamma-ray spectrometry. Aliquots of spent ion-exchange resins and activated charcoal of approximately 5 g were dried in an oven at 60 °C for 24 h [13, 18, 19]. Fractions of around 2 g were then sealed in vials with calibrated geometry for gamma-ray spectrometry measurements in order to determine the activity concentrations [6, 13].

Radiochemical procedures for analysis of difficult to measure nuclides (DTMs)

Only analytical grade reagents and certified calibrated radiation sources were used in the analyses performed in the scope of the radiochemical procedures.

Fractions with 1–2 g of dried spent ion-exchange resins were weighed in beakers of polytetrafluoroethylene (PTFE) and completely dissolved with successive additions of 65 % nitric acid (HNO_3), 30 % hydrogen peroxide (H_2O_2), and 70 % perchloric acid ($HClO_4$). The aliquots were evaporated on a hot plate at 250–300 °C, after each addition, in the following order: (a) twice with 10 mL HNO_3 + 5 mL H_2O_2; (b) once with 10 mL HNO_3 + 5 mL $HClO_4$; (c) once with 10 mL HNO_3 + 5 mL H_2O_2 until white salts were obtained. The salts were dissolved with 8 mol L^{-1} nitric acid (HNO_3) and the volume completed to 100 mL in a volumetric flask. Aliquots for analysis of each radionuclide, except ^{3}H and ^{14}C, were taken from this stock solution [6–8, 13].

Aliquots with 1–2 g of spent activated charcoal were weighed in porcelain crucibles, ashed in an oven at a heating rate of 0.8 °C min^{-1} up to 450 °C, and then maintained at this temperature for 24 h to eliminate most of the organic matter and facilitate the dissolution process. The calcinated aliquots were transferred to PTFE beakers and dissolved following the same procedure used for spent ion-exchange resins samples, except that the same amount of 48 % hydrofluoric acid (HF) replaced the perchloric acid ($HClO_4$), since the spent activated charcoal contains silica in its composition. As before, the resulting salts were dissolved with 8 mol L^{-1} nitric acid (HNO_3) and transferred to a volumetric flask of 100 mL in order to form the stock solution [6–8, 13].

Determination of ^{90}Sr and isotopes of U, Np, Pu, Am and Cm

The determination of activity concentrations of ^{90}Sr and isotopes of actinoid elements was carried out sequentially using a strongly anionic ion-exchange resin (Dowex® 1X8 chloride form, 50–100 mesh, from Sigma Aldrich, Inc.), followed by the specific chromatographic extraction columns with UTEVA®, TRU-Spec and Sr-Spec resins (all from Eichrom Technologies, Inc.). The effluent was evaporated and the residue dissolved in 20 mL of 3 mol L^{-1} HNO_3. The columns were mounted in tandem for percolation of samples, washed with 3 portions, of 5 mL each, of 3 mol L^{-1} HNO_3 and disconnected in the elution process [6, 13].

During a first step, the activity concentrations of ^{237}Np and ^{242}Pu were determined, then of ^{90}Sr, ^{234}U, ^{235}U, ^{236}U, ^{238}U, ^{238}Pu, $^{239+240}$Pu, ^{241}Am and $^{243+244}$Cm [6, 13]. The activity concentrations of ^{239}Pu and ^{240}Pu, as well as the activity concentrations of ^{243}Cm and ^{244}Cm, were expressed together because they are not distinguishable by alpha-particle spectrometry [13, 20].

Regarding detection of Cm isotopes in radioactive wastes, frequently only ^{244}Cm is mentioned [6, 21, 22], because the activity concentration of ^{244}Cm is always much greater than that of ^{243}Cm in spent nuclear fuels [13, 23].

A detailed flow diagram of the radiochemical sequential determination of activity concentrations of ^{90}Sr and isotopes of actinoid elements [13] is shown in Fig. 1.

Determination of ^{55}Fe, ^{59}Ni and ^{63}Ni

Radioanalytical procedures were also employed for the determination of the activity concentrations of ^{55}Fe, ^{59}Ni and ^{63}Ni [7, 8, 13, 18, 24–31]. In summary, they consist of initial precipitation with hydroxides, followed by anionic chromatography to separate Fe and Ni in columns impregnated with dimethylglyoxime (DMG) [31] and measuring by liquid scintillation counting (LSC for ^{55}Fe and ^{63}Ni) and/or by X-ray spectrometry using a low-energy germanium spectrometer (LEGe for ^{55}Fe and ^{59}Ni) [7, 8, 13]. All steps regarding the determination of activity

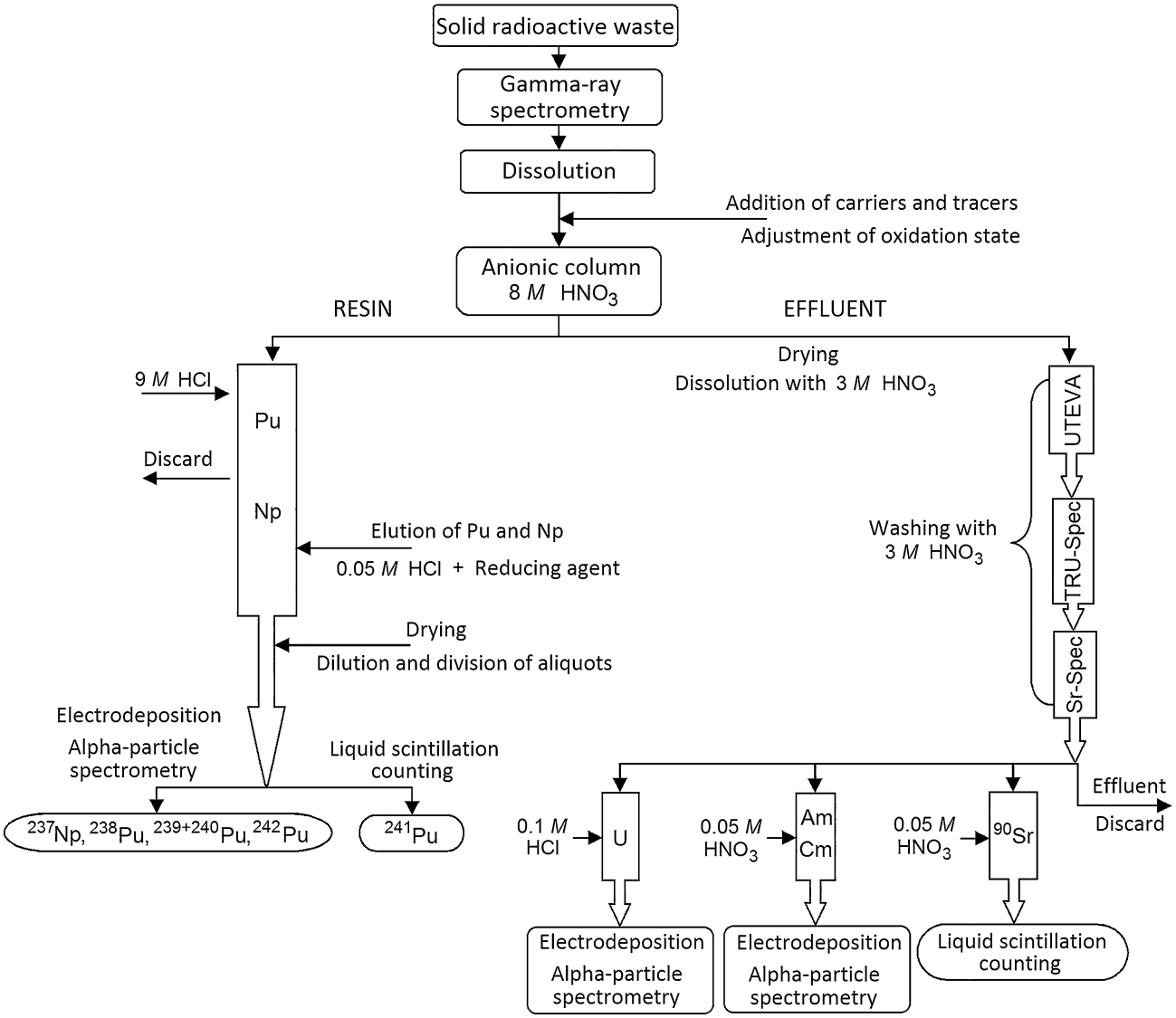

Fig. 1 Flow diagram of the sequential determination of U, Np, Pu, Am, Cm isotopes and ^{90}Sr [13]

concentrations of ^{55}Fe, ^{59}Ni and ^{63}Ni are shown in Fig. 2 using a flow diagram [13].

Determination of ^{3}H and ^{14}C

The radionuclides ^{3}H and ^{14}C were separated from the radioactive waste matrix and from other interfering radionuclides using the Sample Oxidizer 307 (from Perkin-Elmer Life and Analytical Sciences, Inc.), an automatic sample combustion and separation equipment [32].

Aliquots of approximately 0.2 g of wet spent ion-exchange resins or spent activated charcoal samples were mixed with cellulose powder and burned at temperatures 1,000–1,200 °C, under a continuous flow of pure oxygen, to form water and carbon dioxide.

The tritiated water turned into steam, passed through a condenser and was collected in a counting vial in which the reagent Monophase® S is automatically added. The carbon dioxide passed through the condenser and was trapped in a Carbosorb® E (2-methoxy-ethylamine) column to form carbamates that were washed with a washing reagent and collected in counting vials to which 15 mL of the cocktail Permafluor® E were added [32].

Samples of tritiated water and carbon dioxide containing respectively ^{3}H and ^{14}C were then measured by liquid scintillation counting (LSC) for 3,600 s [13] in order to obtain the activity concentrations of these radionuclides. An overall scheme embracing separation of ^{3}H and ^{14}C, as well as determination of their respective activity concentrations [13, 32], is presented in Fig. 3.

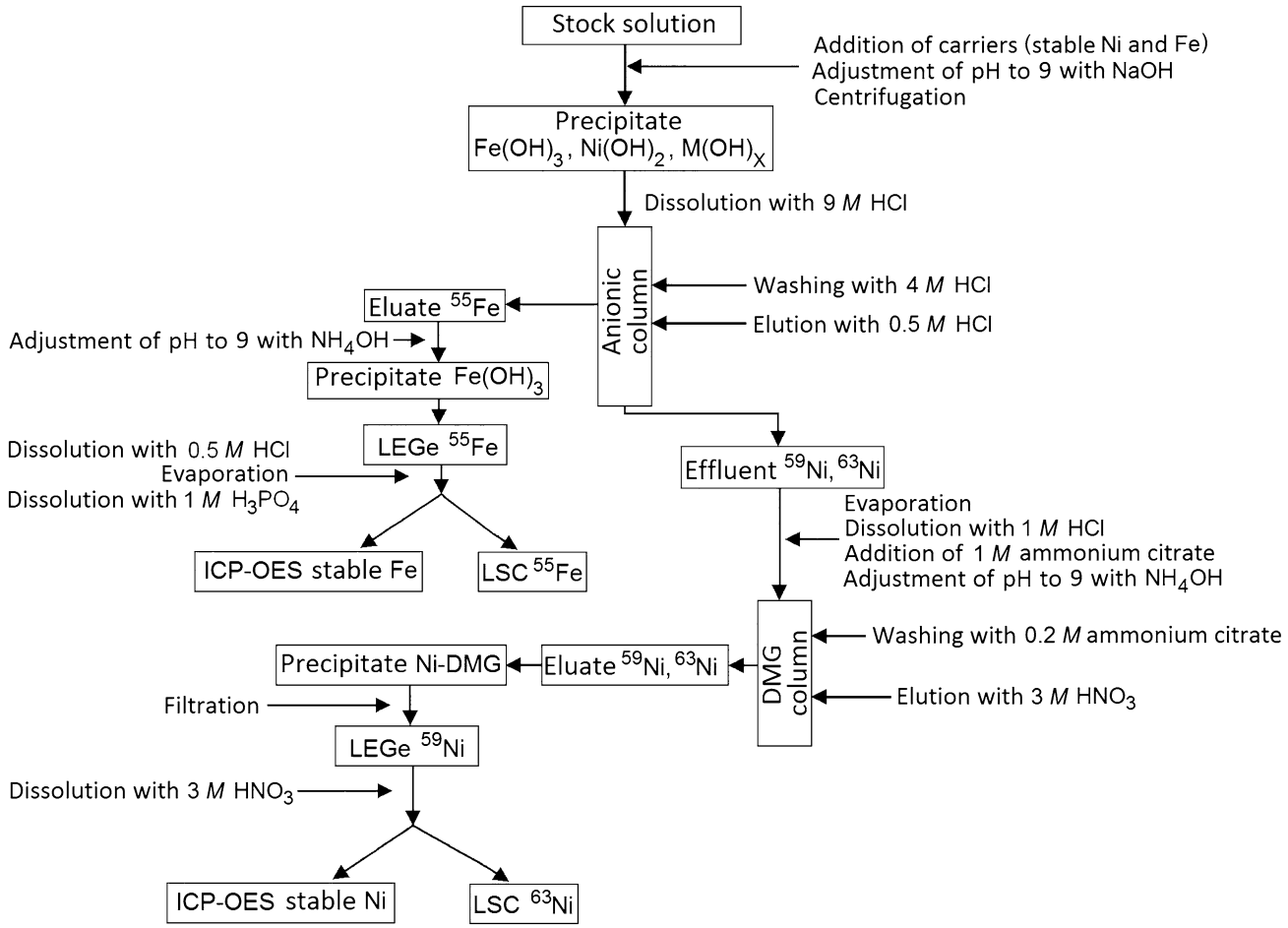

Fig. 2 Flow diagram of the sequential determination of ^{55}Fe, ^{59}Ni and ^{63}Ni [13]

Determination of ^{108m}Ag

The origin of ^{108m}Ag is the activation of the silver–indium–cadmium alloy (Ag–In–Cd alloy in proportion of 80–15–5 % respectively) used in the 4 fork-type control rods of the IEA-R1 nuclear research reactor core and is released to the reactor coolant water through discontinuities in the thin cladding of metallic Ni that coats these rods. The radionuclide ^{108m}Ag is present in the radioactive waste at very low concentrations and although decays by isomeric transition emitting gamma-rays with energies of 433.9, 614.4 and 722.9 keV, direct measurement by gamma-ray spectrometry is difficult due to its low activity [33].

Separation procedure for ^{108m}Ag consists of co-precipitation of silver chloride (AgCl) by addition of silver nitrate ($AgNO_3$) in hydrochloric acid (HCl) solution [34]. An aliquot of 20 mL from the stock solution was mixed with 1 mL 37 % HCl and 1 mL 0.1 N $AgNO_3$ carrier. The AgCl precipitate was filtered on a 4.5 cm diameter cellulose acetate filter with 0.45 μm pore size. The filter containing the AgCl precipitate was dried in a vacuum oven at 60 °C for 2 h and the chemical yield was determined gravimetrically [13]. Next, this filter was wrapped in a thin film of PVC and measured by gamma-ray spectrometry for 30,000 s.

Scaling factor methodology

Scaling factor (SF) is defined as the ratio of A_{DTM} and A_{KN}, which are respectively the activity concentrations of a DTM and of a KN [1, 9, 13, 14, 20, 25, 35–39]:

$$SF = \frac{A_{DTM}}{A_{KN}}. \quad (1)$$

Since the results for this ratio may differ by orders of magnitude, it is necessary to calculate the SF average value as the geometric mean of a series of N measurements [1, 13, 38, 39]:

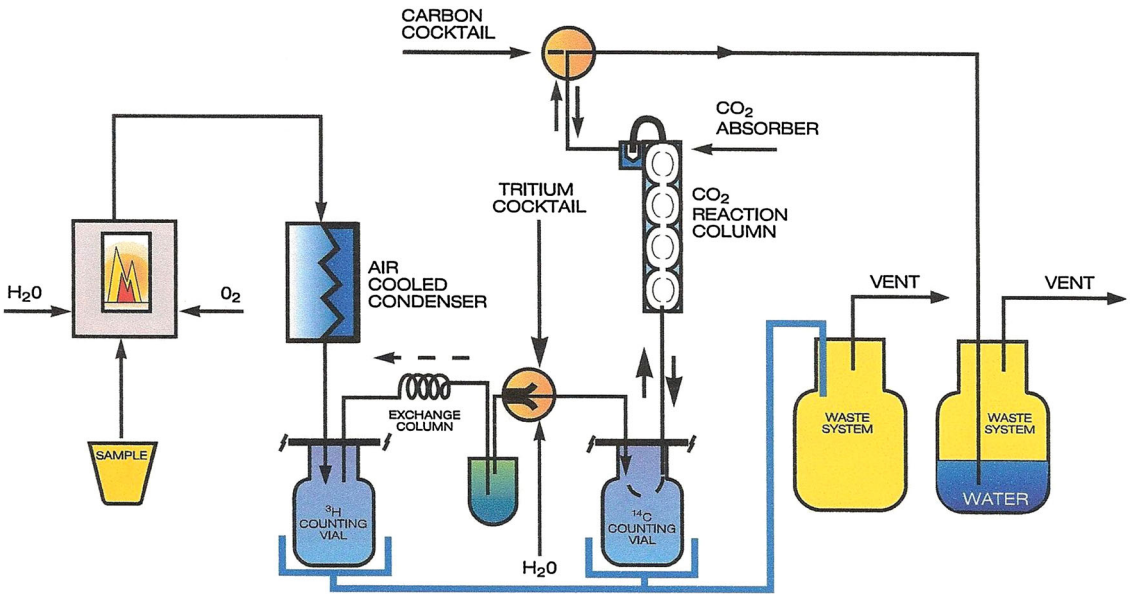

Fig. 3 Diagram of the Perkin-Elmer® Sample Oxidizer 307 equipment [32] employed to measure the activity concentrations of ^{3}H and ^{14}C using the combustion process followed by liquid scintillation counting

$$\overline{\mathrm{SF}} = \mathrm{e}^{\left(\sum_{i=1}^{N} \ln(\mathrm{SF})_i \Big/ N\right)}, \tag{2}$$

whereas the 2σ-dispersion of the results around the geometric mean is calculated by the equation [1, 13, 38, 39]:

$$D_{2\sigma} = \mathrm{e}^{2 \cdot \left(\sqrt{\sum_{i=1}^{N} \left[\ln(\mathrm{SF})_i - \ln(\overline{\mathrm{SF}})\right]^2 \Big/ (N-1)}\right)}. \tag{3}$$

The recommended acceptance criterion for a SF is $D_{2\sigma} \leq 10$ [1, 3], which means that 95.5 % of the measurements results must lie within the range [1, 13, 38–40]:

$$\frac{\overline{\mathrm{SF}}}{10} \leq (\mathrm{SF})_i \leq \overline{\mathrm{SF}} \times 10. \tag{4}$$

When this condition is not satisfied, a correlation function (CF) between the activity concentrations of the DTM and of the corresponding KN is searched, through regression analysis of logarithms, according to the equation [1, 9, 13, 14, 20, 38, 41, 42]:

$$A_{\mathrm{DTM}} = a \cdot (A_{\mathrm{KN}})^{b} \tag{5}$$

that can be rewritten in the form:

$$\ln(A_{\mathrm{DTM}}) = \ln(a) + b \cdot \ln(A_{\mathrm{KN}}), \tag{6}$$

where $\ln(a)$ and b are the regression coefficients. Using the notations $x_i \equiv \ln (A_{\mathrm{KN}})_i$ and $y_i \equiv \ln(A_{\mathrm{DTM}})_i$ in Eq. (6), a measure of the degree of correlation between the two activity concentrations involved is most properly provided by a quantity called the correlation coefficient [13, 43]:

$$r = \frac{\sum_{i=1}^{N} x_i y_i - \frac{\left(\sum_{i=1}^{N} x_i\right) \cdot \left(\sum_{i=1}^{N} y_i\right)}{N}}{\sqrt{\left[\left(\sum_{i=1}^{N} x_i^2 - \frac{\left(\sum_{i=1}^{N} x_i\right)^2}{N}\right) \cdot \left(\sum_{i=1}^{N} y_i^2 - \frac{\left(\sum_{i=1}^{N} y_i\right)^2}{N}\right)\right]}}. \tag{7}$$

The CF is considered acceptable if the correlation coefficient for the fit is $r \geq 0.60$ [1].

However, if the correlation coefficient $r < 0.60$, it is assumed that there is no correlation between the DTM and KN activity concentrations. In this case, the arithmetic mean of the results should be used as an estimate of the DTM activity concentration in that matrix of radioactive waste [1].

In order to obtain statistically significant SFs or CFs for a given representative data set, the recommended number N of $A_{\mathrm{DTM}}/A_{\mathrm{KN}}$ measurements is at least 15 [44] and ideally in the range 20–40 [45].

Results and discussion

The most important features concerning all measurements performed in this work [6–8, 13] (measurement method, sample mass, counting time, minimum detectable activity concentration and chemical yield) are summarized in Table 1.

Table 1 Most important features of the measurements performed in this work: measurement method (LSC—liquid scintillation counting; LEGe—X-ray spectrometry using a low-energy germanium detector; HPGe—gamma-ray spectrometry using a high-purity germanium detector; APS—alpha-particle spectrometry), sample mass, minimum detectable activity concentration (MDA), counting time and chemical yield [6–8, 13]

Radionuclide	Measurement method	Sample mass (g)	MDA (Bq g^{-1})	Counting time (s)	Chemical yield (%)
^{3}H	LSC	1.0	0.1	3,600	100
^{14}C	LSC	1.0	0.5	3,600	100
^{55}Fe	LEGe	0.9	0.5	18,000	64–99
	LSC	0.1	0.021	1,800	64–99
^{59}Ni	LEGe	1.0	0.57	18,000	40–97
^{60}Co	HPGe	1.5	0.030	3,600	100
^{63}Ni	LSC	1.0	5.5	1,800	40–97
^{90}Sr	LSC	1.0	0.5	18,000	62–85
^{108m}Ag	HPGe	1.0	0.17	30,000	≥95
^{137}Cs	HPGe	1.5	0.030	3,600	100
^{234}U, ^{235}U, ^{236}U, ^{238}U	APS	1.0	0.002	200,000	75–99
^{237}Np	APS	1.0	0.002	200,000	60–95
^{238}Pu, $^{239+240}Pu$, ^{242}Pu	APS	1.0	0.002	200,000	60–95
^{241}Pu	LSC	1.0	1.0	18,000	60–95
^{241}Am	APS	1.0	0.002	200,000	45–85
$^{243+244}Cm$	APS	1.0	0.002	200,000	45–85

Although previously selected for the characterization program of radioactive wastes from the IEA-R1 nuclear research reactor, the radionuclides ^{99}Tc, ^{129}I, ^{135}Cs and ^{243}Am were not measured [13]. Mostly, such drawback can be attributed to the fact that ^{99}Tc and ^{129}I are volatile even at temperatures 70–80 °C. As a consequence, it was not possible, concerning these two radionuclides, to use the same sample dissolution procedure (already described in this work) that preceded the radiochemical analysis of almost all other DTMs. Moreover, measurements of activity concentrations of ^{99}Tc, ^{129}I and ^{135}Cs in radioactive wastes with low- and intermediate-activity level require methods beyond radiochemical preparation procedures [38, 39, 46]. These methods consist of neutron activation analysis [47, 48], mass spectrometry [38, 39, 49–51] or both [52], which in our case were neither available nor implemented. In turn, no attempt was made in order to measure the radionuclide ^{243}Am, because the activity concentration of ^{242}Pu—the most direct precursor of ^{243}Am in the chain of nuclear reactions and radioactive decays that forms transuranic elements during nuclear fuel irradiation [13, 53]—resulted below the minimum detectable activity concentration (MDA) in every sample of both radioactive wastes studied.

Measured activities of each radionuclide were corrected, by means of the radioactive decay law, for the exact date of withdrawal (8th January 1993 or 6th November 2003) of the radioactive wastes from the IEA-R1 nuclear research reactor. Final results of the activity concentrations of each radionuclide detected in spent ion-exchange resins and spent activated charcoal are summarized in Fig. 4 by means of a box plot graph [6, 13].

Using the SF methodology, the activity concentrations of DTMs present in the spent ion-exchange resins and spent activated charcoal, removed from the IEA-R1 research reactor in two batches dated to 8th January 1993 and 6th November 2003, were correlated with the activity concentrations of the KNs ^{60}Co and ^{137}Cs.

The average value of the scaling factor ($\overline{SF}$) obtained for each pair DTM/KN and the corresponding 2σ-dispersion are shown in Table 2 for spent ion-exchange resins and in Table 3 for spent activated charcoal [13]. Similarly to the behavior already reported in nuclear power reactors [46, 54], operational changes in the IEA-R1 nuclear research reactor explain most of the variations observed between radioactive waste batches from 1993 and 2003, considered alone or together.

Obtainment of no SFs or CFs at all for tritium (^{3}H) is fully consistent with the accumulated evidence from nuclear power reactors [1, 38, 39, 41, 42, 46]. The predominant chemical form of ^{3}H as tritiated water [55]—also observed in radioactive wastes from the IEA-R1 nuclear research reactor [13]—strongly influences the concentration of ^{3}H and greatly hinders scaling with any KNs.

Regarding ^{14}C, SFs were obtained with both ^{60}Co and ^{137}Cs in the spent activated charcoal, but no correlation was observed in the spent ion-exchange resins, confirming that the activated charcoal is the main adsorber of ^{14}C.

The existence of SFs involving the radionuclide ^{14}C for the two batches of spent activated charcoal is a marked difference from PWRs and BWRs, where usually not even CFs can be obtained in radioactive wastes [1, 38, 39, 41, 42, 46]. While in the IEA-R1 nuclear research reactor C is present in reflectors (graphite blocks with Al cladding)

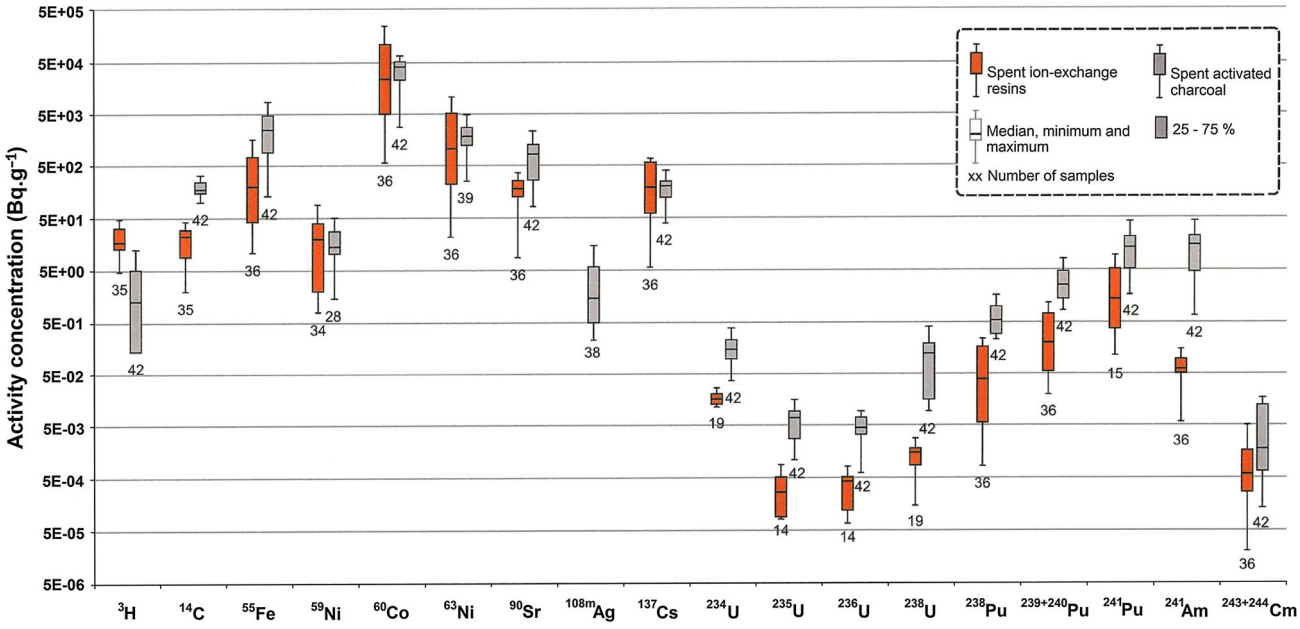

Fig. 4 Activity concentrations of each radionuclide detected in samples of spent activated charcoal and spent ion-exchange resins from the IEA-R1 nuclear research reactor [6, 13]

Table 2 Average value of Scaling Factor ($\overline{SF}$) and 2σ-dispersion ($D_{2\sigma}$) for each DTM/KN pair in spent ion-exchange resins [13]

DTM/KN	1993 + 2003 batches		1993 batch		2003 batch	
	$\overline{SF}$	$D_{2\sigma}$	$\overline{SF}$	$D_{2\sigma}$	$\overline{SF}$	$D_{2\sigma}$
$^{59}Ni/^{60}Co$	3.2×10^{-4}	5.0	4.1×10^{-4}	7.5	2.6×10^{-4}	2.8
$^{59}Ni/^{137}Cs$	4.2×10^{-2}	6.5	4.3×10^{-2}	7.5	3.9×10^{-2}	4.7
$^{63}Ni/^{60}Co$	3.9×10^{-2}	3.9	3.9×10^{-2}	3.8	3.8×10^{-2}	4.1
$^{63}Ni/^{137}Cs$	4.8	4.0	4.1	1.5	5.7	6.7
$^{90}Sr/^{60}Co$	1.2×10^{-2}	16.2	2.3×10^{-2}	4.7	2.4×10^{-3}	14.2
$^{90}Sr/^{137}Cs$	1.1	15.4	2.4	1.7	3.5×10^{-1}	31.8
$^{234}U/^{60}Co$	4.8×10^{-7}	51.3	3.8×10^{-6}	3.9	1.1×10^{-7}	5.4
$^{234}U/^{137}Cs$	5.7×10^{-5}	38.5	3.3×10^{-4}	4.6	1.6×10^{-5}	10.6
$^{235+236}U/^{60}Co$	3.1×10^{-8}	48.0	2.3×10^{-7}	5.6	7.3×10^{-9}	5.4
$^{235+236}U/^{137}Cs$	3.7×10^{-6}	36.0	2.0×10^{-5}	6.5	1.1×10^{-6}	10.0
$^{238}U/^{60}Co$	3.5×10^{-8}	132	4.2×10^{-7}	6.4	4.8×10^{-9}	6.1
$^{238}U/^{137}Cs$	3.7×10^{-6}	88.0	3.6×10^{-5}	7.6	7.2×10^{-7}	9.0
$^{238}Pu/^{60}Co$	8.6×10^{-7}	6.0	8.4×10^{-7}	11.1	8.7×10^{-7}	2.5
$^{238}Pu/^{137}Cs$	1.1×10^{-4}	8.9	8.8×10^{-5}	14.6	1.3×10^{-4}	4.6
$^{239+240}Pu/^{60}Co$	5.8×10^{-6}	3.7	8.9×10^{-6}	3.1	3.8×10^{-6}	2.3
$^{239+240}Pu/^{137}Cs$	7.2×10^{-4}	4.1	9.3×10^{-4}	3.1	5.6×10^{-4}	4.5
$^{241}Pu/^{60}Co$	4.3×10^{-5}	14.4	1.1×10^{-4}	20.5	2.3×10^{-5}	4.9
$^{241}Pu/^{137}Cs$	5.0×10^{-3}	12.0	9.3×10^{-3}	24.1	3.3×10^{-3}	2.5
$^{241}Am/^{60}Co$	1.8×10^{-5}	22.8	1.0×10^{-5}	4.2	4.4×10^{-7}	4.3
$^{241}Am/^{137}Cs$	1.2×10^{-3}	11.8	1.2×10^{-3}	1.7	6.5×10^{-5}	7.0

surrounding the nuclear fuel assemblies in the reactor core, as well as in the activated charcoal of the water polishing system, the absence of graphite or activated charcoal in PWRs and BWRs can explain this difference. In the past, discontinuities in the Al cladding of a few reflectors caused exposure of irradiated graphite to the coolant water of the IEA-R1 nuclear research reactor. However, it should be emphasized that SFs for ^{14}C are expected in radioactive

Table 3 Average value of scaling factor ($\overline{SF}$) and 2σ-dispersion ($D_{2\sigma}$) for each DTM/KN pair in spent activated charcoal [13]

DTM/KN	1993 + 2003 batches		1993 batch		2003 batch	
	$\overline{SF}$	$D_{2\sigma}$	$\overline{SF}$	$D_{2\sigma}$	$\overline{SF}$	$D_{2\sigma}$
$^{14}C/^{60}Co$	8.1×10^{-3}	4.4	8.8×10^{-3}	4.0	6.6×10^{-3}	5.6
$^{14}C/^{137}Cs$	1.4	3.5	1.6	3.5	1.3	3.4
$^{55}Fe/^{60}Co$	6.4×10^{-2}	12.9	1.0×10^{-1}	8.8	2.2×10^{-2}	8.1
$^{55}Fe/^{137}Cs$	12.2	9.1	17.1	7.5	5.7	6.5
$^{59}Ni/^{60}Co$	4.9×10^{-4}	2.7	5.2×10^{-4}	3.0	4.4×10^{-4}	2.1
$^{59}Ni/^{137}Cs$	9.7×10^{-2}	3.9	9.1×10^{-2}	4.0	1.1×10^{-1}	4.0
$^{63}Ni/^{60}Co$	5.5×10^{-2}	3.1	6.0×10^{-2}	2.2	4.4×10^{-2}	5.9
$^{63}Ni/^{137}Cs$	10.7	3.3	10.3	2.3	12.0	7.3
$^{90}Sr/^{60}Co$	1.8×10^{-2}	10.4	3.4×10^{-2}	3.1	4.0×10^{-3}	5.4
$^{90}Sr/^{137}Cs$	3.6	8.1	5.9	3.1	1.0	6.1
$^{108m}Ag/^{60}Co$	5.8×10^{-5}	9.3	3.6×10^{-5}	7.2	1.6×10^{-4}	2.7
$^{108m}Ag/^{137}Cs$	1.1×10^{-2}	10.7	6.1×10^{-3}	5.8	4.2×10^{-2}	2.4
$^{234}U/^{60}Co$	4.0×10^{-6}	10.0	6.9×10^{-6}	5.4	1.0×10^{-6}	2.5
$^{234}U/^{137}Cs$	7.8×10^{-4}	6.4	1.2×10^{-3}	3.9	2.6×10^{-4}	2.3
$^{235}U/^{60}Co$	1.2×10^{-7}	12.0	1.9×10^{-7}	7.8	3.6×10^{-8}	4.2
$^{235}U/^{137}Cs$	2.3×10^{-5}	7.7	3.4×10^{-5}	5.8	9.3×10^{-6}	4.1
$^{236}U/^{60}Co$	1.0×10^{-7}	9.7	1.6×10^{-7}	6.7	3.4×10^{-8}	4.3
$^{236}U/^{137}Cs$	2.0×10^{-5}	6.0	2.8×10^{-5}	4.4	8.8×10^{-6}	4.0
$^{238}U/^{60}Co$	1.9×10^{-6}	29.2	4.8×10^{-6}	6.0	1.8×10^{-7}	2.1
$^{238}U/^{137}Cs$	3.6×10^{-4}	18.9	8.3×10^{-4}	4.5	4.6×10^{-5}	1.8
$^{238}Pu/^{60}Co$	1.8×10^{-5}	7.0	2.6×10^{-5}	5.7	6.8×10^{-6}	2.1
$^{238}Pu/^{137}Cs$	3.5×10^{-3}	4.9	4.6×10^{-3}	4.3	1.7×10^{-3}	2.7
$^{239+240}Pu/^{60}Co$	8.1×10^{-5}	8.6	1.1×10^{-4}	5.7	2.0×10^{-5}	2.1
$^{239+240}Pu/^{137}Cs$	1.5×10^{-2}	5.6	1.8×10^{-2}	3.9	5.0×10^{-3}	2.5
$^{241}Pu/^{60}Co$	3.7×10^{-4}	12.4	6.0×10^{-4}	8.7	9.0×10^{-5}	2.1
$^{241}Pu/^{137}Cs$	7.2×10^{-2}	8.8	1.0×10^{-1}	7.1	2.4×10^{-2}	2.9
$^{241}Am/^{60}Co$	2.3×10^{-5}	9.8	3.7×10^{-5}	6.5	6.7×10^{-6}	2.6
$^{241}Am/^{137}Cs$	4.4×10^{-3}	6.1	6.5×10^{-3}	4.4	1.7×10^{-3}	2.5

wastes from RBMK nuclear power reactors, where graphite is used as moderator [20].

The activation product ^{55}Fe is found mainly in insoluble form in the reactor coolant [4], therefore concentrates more in the spent activated charcoal and, as expected, exhibits SFs with ^{60}Co in both batches of this radioactive waste. However, SFs of ^{55}Fe with ^{137}Cs were also obtained in both batches of the spent activated charcoal and the values of 2σ-dispersions for the SFs with ^{137}Cs were even 15–20 % lower than the corresponding ones for the SFs with ^{60}Co. Moreover, when both waste batches of spent activated charcoal are considered together, the only SF involving ^{55}Fe is obtained with ^{137}Cs. Anyway, the correlations were weak in all cases, with results close to the limit of acceptance.

If both waste batches of spent ion-exchange resins are considered together, only CFs for ^{55}Fe were observed with ^{137}Cs (correlation coefficient $r = 0.61$, slightly above the acceptance criterion $r \geq 0.60$) and with ^{60}Co (correlation coefficient $r = 0.55$, slightly below the acceptance criterion cutoff). These CFs [13] are shown in Fig. 5.

In nuclear power reactors, the DTM ^{55}Fe is always correlated only to the KN ^{60}Co whenever the SF methodology is employed to estimate the inventory of radionuclides in radioactive wastes, since both radionuclides are activation products [1, 38, 39, 46, 54]. Nevertheless, regarding radioactive wastes from the IEA-R1 nuclear research reactor, SFs and CFs involving ^{55}Fe were obtained by means of the SF methodology not only with ^{60}Co, but also with ^{137}Cs, being these last somewhat better [13]. Such unusual result can be understood considering that, beyond production route and physicochemical similarity, also complex transport phenomena affect SFs or CFs involving activity concentrations of radionuclides in radioactive wastes [1]. This is the reason why SFs or CFs are empirically obtained correlations specific for each nuclear facility, operational regime, radioactive waste stream and pair of DTM/KN nuclides.

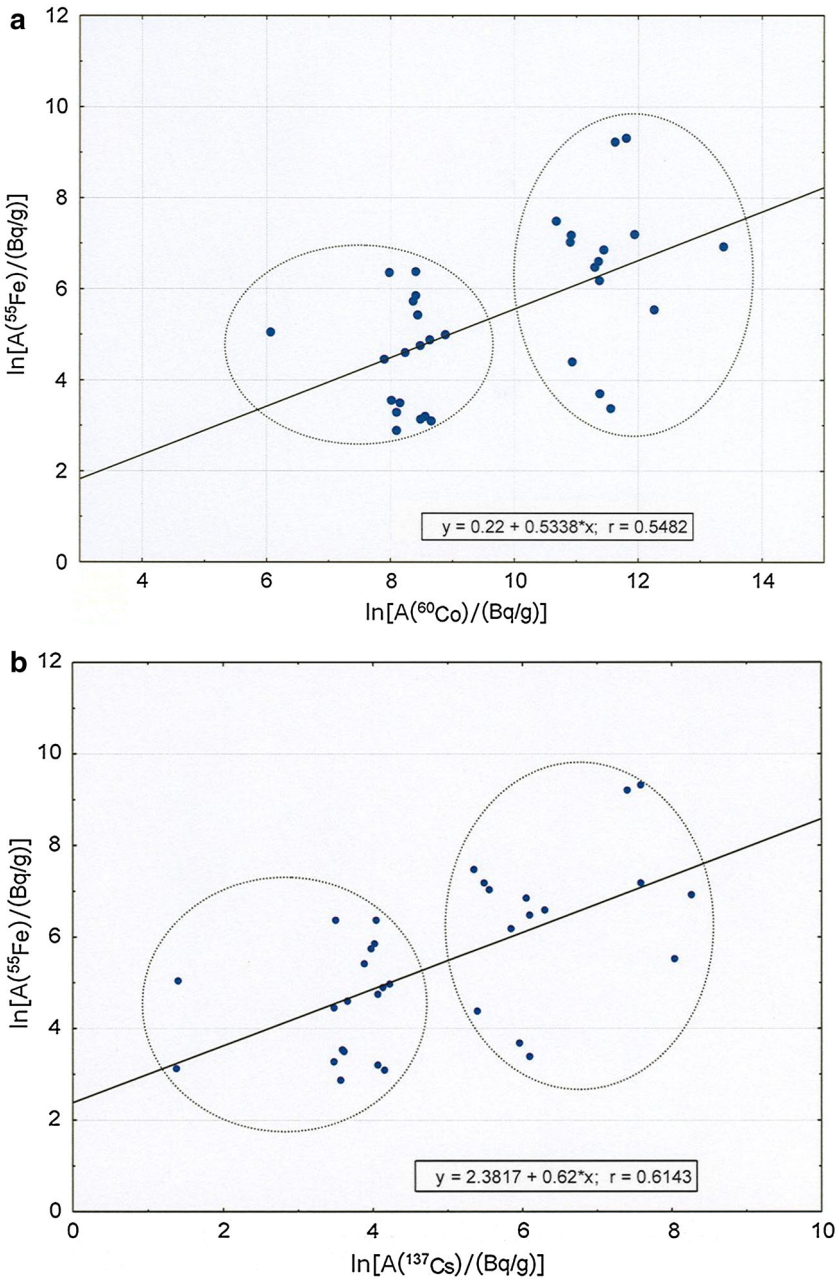

Fig. 5 Correlation functions (CFs) obtained in spent ion-exchange resins from the IEA-R1 nuclear research reactor, fitting the data of the activity concentrations ratio of ^{55}Fe with **a** ^{60}Co and **b** ^{137}Cs; encircled areas indicate data corresponding to the 1993 batch (*left*) and to the 2003 batch (*right*), whereas the main parameters of each fit are presented [13]

Radioactive isotopes of Ni and Co present in both radioactive wastes originate predominantly from the neutron activation of the thin cladding of metallic Ni that coats the control rods of the IEA-R1 nuclear research reactor [8]. These chemical elements are also relatively insoluble so, as expected, SFs were found both in the spent activated charcoal and in the spent ion-exchange resins, most often with relatively low 2σ-dispersion. Moreover, SFs were also observed with ^{137}Cs. It is worth noting that the average value of the scaling factor ($\overline{SF}$) varied little between the two waste types and the two waste batches.

The observed stability of the average value of the scaling factor ($\overline{SF}$) for ^{63}Ni/^{60}Co and ^{59}Ni/^{60}Co is in remarkable agreement with a trend already observed in radioactive wastes from nuclear power reactors, in which the SFs for these pairs are considered valid for all radioactive waste generated in a specific nuclear reactor [39]. This fact is an evidence of a common origin of the Ni and

Table 4 Average value of scaling factor ($\overline{SF}$), 2σ-dispersion ($D_{2\sigma}$) and number of analyzed samples (N) for $^{63}Ni/^{60}Co$ and $^{59}Ni/^{60}Co$ in spent ion-exchange resins from the IEA-R1 nuclear research reactor and from several nuclear power reactors of the USA [13, 39]

DTM/KN	IEA-R1	BWRs	PWRs
$^{63}Ni/^{60}Co$			
$\overline{SF}$	0.039	0.022	0.63
$D_{2\sigma}$	3.9	7.4	6.3
N	36	326	301
$^{59}Ni/^{60}Co$			
$\overline{SF}$	0.00032	0.00057	0.012
$D_{2\sigma}$	5.0	7.8	3.1
N	34	62	63

Co isotopes, which in the case of the IEA-R1 nuclear research reactor is the thin cladding of metallic Ni that coats its control rods [8].

As already emphasized in this work, every nuclear reactor has distinct SFs and/or CFs. However, a comparison between the average value of the scaling factor ($\overline{SF}$) obtained for the pairs $^{63}Ni/^{60}Co$ and $^{59}Ni/^{60}Co$ in spent ion-exchange resins from the IEA-R1 nuclear research reactor [13] and from several light-water nuclear power reactors [39] reveals close proximity with results achieved in radioactive wastes from boiling water reactors (BWRs), as can be seen in Table 4 that presents data for 44 pressurized water reactors (PWRs) and 23 BWRs, measured between 1984 and 1999 in the USA [39]. However, no such comparison is possible for activated charcoal, since it is not used in nuclear power reactors.

The differences between the average value of the scaling factor ($\overline{SF}$) obtained in BWRs and PWRs are attributed to the fact that the main source of Ni and Co radioisotopes in PWRs is the steam generator tubes [41], while in BWRs the stainless steel lining of the boron carbide (B_4C) control rods [56] is probably such a source, a feature slightly similar to the IEA-R1 nuclear research reactor. Until recently, the tubes of the steam generators used in many PWRs were made of Inconel® 600, an alloy containing 72 % Ni [57] that showed stress corrosion cracking. As a consequence, several nuclear power plants worldwide were forced to replace the steam generators [58].

In aqueous medium, ^{90}Sr is usually dissolved. However, in slightly alkaline solutions, this radionuclide can be in the form of insoluble carbonate. In either of these two chemical forms, it was expected the existence of a SF with ^{137}Cs, as both are fission products. Considered together, the two waste batches of activated charcoal presented this SF, but also when each batch was evaluated separately. In spent ion-exchange resins, however, neither SFs nor CFs were obtained, except for the 1993 batch, in which SFs were obtained with ^{60}Co and with ^{137}Cs, the 2σ-dispersion being lower for ^{137}Cs. This behavior is similar to that observed in radioactive wastes from nuclear power reactors, in which 2σ-dispersions are slightly smaller for ^{137}Cs than for ^{60}Co [39], but not rarely otherwise [1, 39] due to two characteristics that ^{90}Sr and ^{60}Co have in common: the predominant formation in the surface layers of components in the reactor core and the low solubility [1].

The SFs obtained for the pairs $^{90}Sr/^{60}Co$ and $^{90}Sr/^{137}Cs$ in both radioactive wastes presented 2σ-dispersion much lower in the 1993 than in the 2003 batch, for which SFs or CFs were not even found in spent ion-exchange resins. Notably for the pair $^{90}Sr/^{60}Co$, this result can be explained by the significant differences that exist between ^{90}Sr and ^{60}Co chemical behavior and becomes even more evident during changes of reactor operation power accomplished in a short period of time (transient), as observed in PWRs in France [38]. Therefore, the marked difference of SFs for $^{90}Sr/^{60}Co$ between the 1993 and the 2003 batches, mainly on spent ion-exchange resins, reveals the contrast between the regularity of the operation of the IEA-R1 nuclear research reactor up to 1993 (operation power of 2 MW during business hours) and the variation of the operating regime of this reactor led mainly after 1995 (operation power varying between 3 and 5 MW for 64 consecutive hours weekly).

In the spent ion-exchange resins, ^{108m}Ag activity was always below the MDA. However, in spent activated charcoal, SFs for ^{108m}Ag with ^{60}Co and with ^{137}Cs were obtained for each waste batch, the lowest 2σ-dispersion being that with ^{137}Cs.

The radionuclide ^{108m}Ag constitutes a special case in this work, because it was the only DTM with a sharp increase in the average value of the scaling factor ($\overline{SF}$) from the 1993 to the 2003 batch, while the overall trend for all the other radionuclides was decrease. However, this seemingly anomalous behavior is consistent with evidences revealed during inspections performed in 1998, 2000 and 2001 on all control rods of the IEA-R1 nuclear research reactor using a radiation-resistant underwater camera, which showed clearly flaking and pit corrosion of their thin Ni cladding [59]. This behavior is also consistent with gamma-ray spectrometry measurements performed inside the IEA-R1 reactor pool that detected ^{110m}Ag [60–63]. These facts led to the replacement of the IEA-R1 reactor control rods in 2003.

The U isotopes presented acceptable SFs with ^{60}Co and ^{137}Cs for the two waste batches of spent activated charcoal, either considered together or separately. Exceptions were ^{235}U, for which no SF was obtained with ^{60}Co, as well as ^{238}U, for which no SF was obtained for the waste batches taken together. In spent activated charcoal, the activity of the U isotopes correlates better with ^{137}Cs.

Table 5 Scaling factor (SF) or correlation function (CF) obtained in radioactive wastes of the IEA-R1 nuclear research reactor [13]

DTM	Spent activated charcoal			Spent ion-exchange resins		
	1993+2003 batches	1993 batch	2003 batch	1993+2003 batches	1993 batch	2003 batch
^{3}H	No SF or CF	No SF or CF	No SF or CF	No SF or CF	No SF or CF	No SF or CF
^{14}C	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	No SF or CF	No SF or CF	No SF or CF
^{55}Fe	SF with ^{137}Cs	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	CF with ^{60}Co and ^{137}Cs	No SF or CF	No SF or CF
^{59}Ni	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs
^{63}Ni	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs
^{90}Sr	SF with ^{137}Cs	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	No SF or CF	SF with ^{60}Co and ^{137}Cs	No SF or CF
^{108m}Ag	SF with ^{60}Co	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	< MDA*	< MDA*	< MDA*
^{234}U	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	No SF or CF	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co
^{235}U	SF with ^{137}Cs	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	No SF or CF	No SF or CF	No SF or CF
^{236}U	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	No SF or CF	No SF or CF	No SF or CF
$^{235+236}U$	–	–	–	No SF or CF	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs
^{238}U	No SF or CF	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	No SF or CF	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs
^{238}Pu	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	No SF or CF	SF with ^{60}Co and ^{137}Cs
$^{239+240}Pu$	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs
^{241}Pu	SF with ^{137}Cs	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	No SF or CF	No SF or CF	SF with ^{60}Co and ^{137}Cs
^{241}Am	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs	No SF or CF	SF with ^{60}Co and ^{137}Cs	SF with ^{60}Co and ^{137}Cs
$^{243+244}Cm$	No SF or CF	No SF or CF	No SF or CF	No SF or CF	No SF or CF	No SF or CF

*MDA = minimum detectable activity concentration.

In the spent ion-exchange resins, the activity concentration of U isotopes is much lower and SFs were obtained with ^{60}Co and ^{137}Cs only considering the waste batches separately and, even so, with exceptions: for the 2003 waste batch, no SF was obtained for ^{234}U or $^{235+236}$U with ^{137}Cs. Some SFs for the U isotopes showed lower 2σ-dispersion with ^{137}Cs and others with ^{60}Co.

Generally, acceptable SFs were obtained in spent activated charcoal for the Pu isotopes with ^{60}Co and ^{137}Cs. The only exception was the pair ^{241}Pu/^{60}Co for the waste batches taken together. The SFs for $^{239+240}$Pu with ^{137}Cs and ^{60}Co presented the lowest 2σ-dispersions. A larger difference was observed between the waste batches of spent ion-exchange resins, in which the ^{238}Pu activity concentration is very low and no SFs were obtained in the 1993 waste batch. However, SFs were obtained in the 2003 waste batch for ^{241}Pu with both ^{137}Cs and ^{60}Co.

Concerning spent activated charcoal, SFs for ^{241}Am with ^{60}Co and ^{137}Cs were obtained in waste batches considered separately or jointly, whereas in the spent ion-exchange resins this occurred only for each waste batch separately.

Finally, no SFs or CFs at all were obtained for the pairs $^{243+244}$Cm/^{60}Co and $^{243+244}$Cm/^{137}Cs, mainly due to the very low activity concentrations of Cm isotopes, usually slightly larger than the MDA of 0.002 Bq g^{-1} for alpha-particle spectrometry in spent ion-exchange resins and in spent activated charcoal from the IEA-R1 nuclear research reactor. The same occurred with ^{237}Np and ^{242}Pu, which were always below the respective MDAs.

An overview embracing all SFs and CFs obtained [13] for the most important radioactive wastes with low- and intermediate-activity level from the IEA-R1 nuclear research reactor is shown in Table 5.

Conclusion

The SF methodology was employed successfully for assay of radioactive wastes with low- and intermediate-activity level generated in a nuclear research reactor. This enabled spent ion-exchange resins and spent activated charcoal, both removed from the IEA-R1 nuclear research reactor along 46 years of operation, to be characterized regarding the radionuclide inventory, whereas exposure to ionizing radiation, contamination risks and operational costs, inherent to this kind of routine work, have been drastically reduced.

As a whole, 26 radionuclides were selected for research in this work, taking into account design, history and operational features of the IEA-R1 nuclear research reactor. Many radiochemical procedures used in separation of almost all these radionuclides were developed or adapted and implemented, based in processes of combustion, co-precipitation, extraction chromatography and ion-exchange chromatography, as well as diverse forms of preparation of sources for measurements by alpha-particle spectrometry, liquid scintillation counting, gamma-ray spectrometry and/or X-ray spectrometry. The good results, obtained as to recovery of tracers and reproducibility of measurements, indicate that these radiochemical procedures can be used during routine determination of activity concentrations of radionuclides in radioactive wastes.

In the spent ion-exchange resins and/or the spent activated charcoal, embracing all 21 drums of both batches (dated to 1993 and 2003) of radioactive wastes already stored at the IPEN/CNEN-SP, activity concentrations surpassing the MDA were measured for 18 DTMs (^{3}H, ^{14}C, ^{55}Fe, ^{59}Ni, ^{63}Ni, ^{90}Sr, ^{108m}Ag, ^{234}U, ^{235}U, ^{236}U, ^{238}U, ^{238}Pu, $^{239+240}$Pu, ^{241}Pu, ^{241}Am and $^{243+244}$Cm) and for two KNs (^{60}Co and ^{137}Cs).

However, in the scope of this work, the methods of neutron activation analysis and mass spectrometry, necessary to measure activity concentrations of three DTMs previously selected for research (^{99}Tc, ^{129}I and ^{135}Cs), were not available or implemented. Moreover, no attempt was made in order to measure the activity concentration of another previously selected DTM (^{243}Am), because the MDA of its most direct precursor in the transuranic elements formation chain (^{242}Pu) was never attained in both radioactive wastes studied.

From all the mentioned radionuclides, SFs or CFs corresponding to DTM/KN pairs have been obtained in at least one of the radioactive wastes studied for 15 DTMs (^{14}C, ^{55}Fe, ^{59}Ni, ^{63}Ni, ^{90}Sr, ^{108m}Ag, ^{234}U, ^{235}U, ^{236}U, ^{238}U, ^{238}Pu, $^{239+240}$Pu, ^{241}Pu and ^{241}Am).

An interesting result of this work is that the average value of the scaling factor ($\overline{SF}$) and the 2σ-dispersion ($D_{2\sigma}$) for ^{63}Ni/^{60}Co and ^{59}Ni/^{60}Co pairs obtained in spent ion-exchange resins from the IEA-R1 nuclear research reactor (a MTR-type research reactor) indicate a variation of these DTM/KN ratios within a range fully compatible with corresponding ones obtained in spent ion-exchange resins from 23 boiling water reactors (nuclear power BWRs) of the USA. Such evidence may be explained by the fact that the main source of Ni and Co radioisotopes in BWRs is probably the stainless steel lining of the boron carbide (B_4C) control rods, a feature slightly similar to the IEA-R1 nuclear research reactor, in which this source is the thin cladding of metallic Ni that coats its control rods.

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References

1. IAEA, International Atomic Energy Agency (2009) Determination and use of scaling factors for waste characterization in nuclear power plants. Nuclear Energy Series No. NW-T-1.18. Vienna
2. Bickel M, Holmes L, Janzon C, Koulouris G, Pilviö R, Slowikowski B, Hill C (2000) Radiochemistry: inconvenient but indispensable. Appl Radiat Isot 53:5–11
3. U. S. NRC, United States Nuclear Regulatory Commission (1982) Licensing requirements for land disposal of radioactive waste. Code of Federal Regulations, 10CFR61. Office of Federal Register, Washington D.C.
4. Lin CC (1996) Radiochemistry in nuclear power reactors. Committee on Nuclear and Radiochemistry, Commission on Physical Sciences, Mathematics, and Applications, National Research Council, National Academy Press, Washington D.C.
5. CNEN, Comissão Nacional de Energia Nuclear (2002) Critérios de Aceitação para Deposição de Rejeitos Radioativos de Baixo e Médio Níveis de Radiação. CNEN-NN-6.09. Rio de Janeiro
6. Taddei MHT, Vicente R, Marumo JT, Sakata SK, Terremoto LAA (2013) Determination of long-lived radionuclides in radioactive wastes from the IEA-R1 nuclear research reactor. J Radioanal Nucl Chem 295:951–957
7. Taddei MHT, Macacini JF, Vicente R, Marumo JT, Sakata SK, Terremoto LAA (2013) A comparative study using liquid scintillation counting and X-ray spectrometry to determine ^{55}Fe in radioactive wastes. J Radioanal Nucl Chem 295:2267–2272
8. Taddei MHT, Macacini JF, Vicente R, Marumo JT, Sakata SK, Terremoto LAA (2013) Determination of ^{63}Ni and ^{59}Ni in spent ion-exchange resin and activated charcoal from the IEA-R1 nuclear research reactor. Appl Radiat Isot 77:50–55
9. ISO, International Organization for Standardization (2007) Nuclear energy–nuclear fuel technology–scaling factor method to determine the radioactivity of low- and intermediate-level radioactive waste packages generated at nuclear power plants. ISO 21238:2007(E)
10. Perrotta JA, Terremoto LAA, Zeituni CA (1998) Experience on wet storage spent fuel sipping at IEA-R1 Brazilian research reactor. Ann Nucl Energy 25:237–258
11. Vasconcellos MBA, Saiki M, Fávaro DIT, Maihara VA, Figueiredo AMG, Catharino MGM (2004) Neutron activation analysis at the research reactor center of IPEN/CNEN-SP—biological and environmental applications. J Radioanal Nucl Chem 259:489–492
12. Vasconcellos MBA, Saiki M (2006) Radiochemistry teaching and research activities in Brazil. J Radioanal Nucl Chem 270:263–267
13. Taddei MHT (2013) Determinação de Fatores de Escala para Estimativa do Inventário de Radionuclídeos em Rejeitos de Média e Baixa Atividades do Reator IEA-R1. Doctoral Thesis. IPEN/CNEN-SP, São Paulo
14. IAEA, International Atomic Energy Agency (2007) Strategy and methodology for radioactive waste characterization. IAEA-TECDOC-1537. Vienna
15. Reis AS Jr, Temba ESC, Kastner GF, Monteiro RPG (2011) Combined procedure using radiochemical separation of plutonium, americium and uranium radionuclides for alpha-spectrometry. J Radioanal Nucl Chem 287:567–572
16. Oliveira TC, Monteiro RPG, Oliveira AH (2011) A selective separation method for ^{93}Zr in radiochemical analysis of low and intermediate level wastes from nuclear power plants. J Radioanal Nucl Chem 289:497–501
17. Temba ESC, Reis AS Jr, Amaral AM, Monteiro RPG (2011) Separation and determination of ^{90}Sr in low- and intermediate-level radioactive wastes using extraction chromatography and LSC. J Radioanal Nucl Chem 290:631–635
18. Gresits I, Tölgyesi S (2003) Determination of soft X-ray emitting isotopes in radioactive liquid wastes of nuclear power plants. J Radioanal Nucl Chem 258:107–112
19. Alcalá MR (1997) Análisis de Radionucleidos Emisores de Radiación Beta Presentes en Residuos Radiactivos Procedentes de Centrales Nucleares, Mediante Centelleo en Fase Líquida. Doctoral Thesis, Universidad Complutense de Madrid, Facultad de Ciencias Químicas, Departamento de Química Analítica, Madrid
20. Remeikis V, Plukis A, Juodis L, Gudelis A, Lukauskas D, Druteikienė R, Lujanienė G, Lukšienė B, Plukienė R, Duškesas G (2009) Study of the nuclide inventory of operational radioactive waste for the RBMK-1500 reactor. Nucl Eng Des 239:813–818
21. Gáscon JL, Aceña ML, Suárez JA, Rodríguez M (1994) Radiochemical methods for the determination of plutonium, americium and curium in typical waste streams. J Alloy Compd 213(214):557–559
22. Rodríguez M, Gáscon JL, Suárez JA (1997) Study of interferences in the determination of Pu, Am and Cm in radioactive waste by extraction chromatography. Talanta 45:181–187
23. Culbreth B, Bakker E, Viggato J (2002) The fission properties of curium separated from spent nuclear fuel. Technical Report. University of Nevada, Las Vegas
24. Kaye JH, Strebin RS, Nevissi AE (1994) Measurement of ^{63}Ni in highly radioactive Hanford waste by liquid scintillation counting. J Radioanal Nucl Chem 180:197–200
25. Niese S, Boden W (1995) Scaling factors for activated corrosion products in low-level-wastes from power reactors. J Radioanal Nucl Chem 198:161–167
26. Navarrete M, Cabrera L, Martínez T, Llaven H (1995) Separation of ^{63}Ni traces from low and medium level radioactive wastes produced during the operation of nuclear power reactors. J Radioanal Nucl Chem 199:493–497
27. Hou X, Østergaard LF, Nielsen SP (2005) Determination of ^{63}Ni and ^{55}Fe in nuclear wastes samples using radiochemical separation and liquid scintillation counting. Anal Chim Acta 535:297–307
28. Warwick PE, Croudace IW (2006) Isolation and quantification of ^{55}Fe and ^{63}Ni in reactor effluents using extraction chromatography and liquid scintillation analysis. Anal Chim Acta 567:277–285
29. Fišera O, Šebesta F (2010) Determination of ^{59}Ni in radioactive waste. J Radioanal Nucl Chem 286:713–717
30. Rosskopfová O, Galamboš M, Rajec P (2011) Determination of ^{63}Ni in low level solid radioactive waste. J Radioanal Nucl Chem 289:251–256
31. Lehto J, Hou X (2011) Chemistry and analysis of radionuclides: laboratory techniques and methodology. Wiley, New York
32. Perkin-Elmer® Inc. (2003) Sample Oxidizer Model 307—operation manual. Manual Reorder No. 1694057. Shelton, CT
33. Bihari Á, Szücs Z, Mogyorósi M, Pintér T (2010) Combined determination of ^{99}Tc and ^{108m}Ag in L/ILW liquid wastes. J Radioanal Nucl Chem 286:759–763
34. Kolthoff IM, Sandell EB, Meehan EJ, Bruckenstein S (1969) Quantitative chemical analysis. The Macmillan Publishing Co., London
35. Niese S, Gleisberg B (1995) Determination of radioisotopes of Ce, Eu, Pu, Am and Cm in low-level wastes from power reactors. J Radioanal Nucl Chem 200:31–41
36. Niese S, Gleisberg B (1996) Determination of radioisotopes of Ce, Eu, Pu, Am and Cm in low-level wastes from power reactors using low-level measuring techniques. Appl Radiat Isot 47:1113–1114

37. IAEA, International Atomic Energy Agency (1997) Characterization of Radioactive Waste Forms and Packages. IAEA Technical Reports Series No. 383. Vienna
38. EPRI, Electric Power Research Institute (1996) Low level waste characterization guidelines. TR-107201. Palo Alto, CA
39. EPRI, Electric Power Research Institute (1999) Utility use of constant scaling factors. TR-109448. Palo Alto, CA
40. U. S. NRC, United States Nuclear Regulatory Commission (1983) Low-level waste licensing branch technical position on radioactive waste classification. Washington D.C.
41. Raymond A, Müller W, Gens R, Gili M, Morales A, Yates A (1995) Inventory and characterization of important radionuclides for the safety of storage and disposal: correlation with key radionuclides in typical waste streams. J Radioanal Nucl Chem 193:377–390
42. Raymond A, Lagarde B, Pitiot A (1996) Studies on important radionuclides for the safety of a radioactive waste disposal site: correlation between easily measurable gamma emitters and long-lived radionuclides. Nucl Technol 115:192–197
43. Chatfield C (1978) Statistics for technology—a course in applied statistics. Chapman and Hall Ltd., London
44. Noé M, Müller W, Gens R, Gili M, Morales A, Yates A, Ormai P (1998) Development of methods to provide an inventory of radiologically relevant radionuclides: analytical methods and correlation of data. European Commission Report. Nuclear Science and Technology. Final Report EUR 17978. ISBN 92-828-2145-5. Luxembourg
45. Kashiwagi M, Müller W, Lantés B (2000) Considerations on the activity concentration determination method for low-level waste packages and nuclide data comparison between different countries. IAEA International Conference on the Safety of Radioactive Waste Management. IAEA-CN-78/43. Cordoba
46. EPRI, Electric Power Research Institute (2003) Operational changes & impacts on LLW scaling factors. TR-1008017. Palo Alto, CA
47. Chao JH, Tseng CL (1996) Determination of ^{135}Cs by neutron activation analysis. Nucl Instrum Methods A 372:275–279
48. Chao JH, Tseng CL, Lee CJ, Hsia CC, Teng SP (1999) Analysis of I-129 in radwastes by neutron activation. Appl Radiat Isot 51:137–143
49. Meeks AM, Giaquinto JM, Keller JM (1998) Application of ICP-MS radionuclide analysis to "Real World" samples of Department of Energy radioactive waste. J Radioanal Nucl Chem 234:131–135
50. Pibida L, Nörterhäuser W, Hutchinson JMR, Bushaw BA (2001) Evaluation of resonance ionization mass spectrometry for the determination of ^{135}Cs/^{137}Cs isotope ratios in low-level samples. Radiochim Acta 89:161–168
51. Chao JH, Tseng CL, Lee CJ (2002) Sequential extraction separation for determination of technetium-99 in radwastes by ICP-MS. J Radioanal Nucl Chem 251:105–112
52. Strebin RS, Brauer FP, Kaye JH, Rapids MS, Stoffels JJ (1988) Neutron activation and mass spectrometric measurement of ^{129}I. J Radioanal Nucl Chem 127:59–73
53. Bailly H, Ménessier D, Prunier C (eds) (1999) The nuclear fuel of pressurized water reactors and fast reactors—design and behaviour. Intercept Ltd., Andover
54. James DW (2004) Impacts of operational changes on LLW scaling factors. WM'04 Conference, WM-4606. Tucson, AZ
55. Selleslagh E (1976) Management of the tritium produced by nuclear power plants. Health Phys 31:279
56. Lepel EA, Pratt SL, Robertson DE, Thomas CW, Haggard DL (1995) Radiological characterization of spent control rod assemblies. J Radioanal Nucl Chem 194:81–94
57. Was GS, Tischner HH, Latanision RM (1981) The influence of thermal treatment on the chemistry and structure of grain boundaries in Inconel 600. Metall Trans A 12:1397–1408
58. ELETRONUCLEAR, Eletrobrás Termonuclear SA (2009) Angra 1—Substituição e Armazenamento dos Geradores de Vapor. Rio de Janeiro
59. Silva JER, Terremoto LAA, Castanheira M, Zeituni CA, Damy MA (2002) Inspeções Visuais nas Barras Absorvedoras de Nêutrons do Reator IEA-R1. XIII Encontro Nacional de Física de Reatores e Termohidráulica (XIII ENFIR), International Nuclear Atlantic Conference (INAC), Rio de Janeiro
60. Terremoto LAA, Zeituni CA, Perrotta JA, Silva JER (2000) Gamma-ray spectroscopy on irradiated MTR fuel elements. Nucl Instrum Methods A 450:495–514
61. Terremoto LAA, Zeituni CA, Perrotta JA, Silva AT, Silva JER (2002) Teste de Sipping em um Elemento Combustível Tipo Placa Falhado. XIII Encontro Nacional de Física de Reatores e Termohidráulica (XIII ENFIR), International Nuclear Atlantic Conference (INAC), Rio de Janeiro
62. Zeituni CA, Terremoto LAA, Silva JER (2004) Sipping tests on a failed irradiated MTR fuel element. PHYSOR 2004: the physics of fuel cycles and advanced nuclear systems—global developments. American Nuclear Society (ANS), Chicago
63. Zeituni CA, Terremoto LAA, Silva JER (2004) Failed MTR fuel element detect in a sipping tests. Americas Nuclear Energy Symposium (ANES). OSTI ID: 841352. Miami