Radiochemical characterization of spent filter cartridges from the primary circuit of a research reactor

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Abstract

Radiochemical-based analyses have been used for the characterization of radioactive waste. Nevertheless, the determination of alpha, beta and gamma emitters by radiochemical analysis of spent cartridge filters from a swimming-pool type reactor has not been previously addressed. This work aims at identifying and quantifying the radionuclides present in this waste, including the difficult to measure radionuclides. The distribution of the radionuclides in the filter was investigated by the determination of gamma-emitting nuclides and the z-score of the measured activity concentrations. The results indicated that all the filters are homogeneous, meeting the homogeneity criteria recommended by the International Atomic Energy Agency.

Keywords Cartridge filters · Radiochemistry · Difficult to measure radionuclides · Solid radioactive waste

Introduction

IEA-R1 reactor is operated by the Nuclear and Energy Research Institute (IPEN), at the campus of the University of São Paulo, Brazil since 1957. This facility is an open pool-type nuclear research reactor, operating at 2–5 MW, and uses light water as a coolant, moderator, and biological shield [1]. The main activities developed in the facility are nuclear physics, materials research, production of radioisotopes, and gamma and neutron irradiation of samples [2].

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Polypropylene filter cartridges remove suspended solid materials from the cooling water during the operation of the reactor and become radioactive waste as they are replaced [3]. Quality control of the water indicates the necessity of periodic replacement of these filters. After the appropriate time for the decay of very short-lived isotopes, the filters are transported to the Radioactive Waste Management Department facility (SEGRR) at IPEN, for interim storage and treatment. The SEGRR is responsible for all the steps of management, except disposal, of the radioactive waste generated by IPEN and of the waste received from many radioisotope users in the country. The disposal facility is presently under siting and implementation by another organization in Brazil.

Formerly, the filters were drummed and compacted at the SEGRR without any concerns about the inventory. However, present regulations require that the radioactive content of each drum be determined and stated in the documents for shipping the waste to a disposal facility [4, 5].

There are a number of techniques that are currently being used to determine the radioisotope content of waste packages. However, the choice of the most suitable method depends on factors such as type of radiation emitted, the costs and availability of measuring instruments, the dose rates involved in taking and handling waste samples, the physical state and the homogeneity of the waste, among others [6].

Replacement of the filters from the reactor's water treatment system generates about 36 units annually with initial contact dose rates in the order of hundreds of millisievert per hour. Therefore, for the SEGRR to routinely determine the radioactive inventory of these filters, it is preferred an accurate method of characterization, which does not need sampling and laboratory analysis.

Waste from nuclear reactors contains fission and activation products and transuranic elements, only a few of them emitting gamma radiation measurable by simple gamma spectrometry of the waste package. The radionuclides whose concentrations cannot be measured by direct gamma spectrometry are called difficult to measure (DTM).

In routine waste management activities, the concentrations of the DTM can preferably be estimated by indirect methods, such as scaling factors (SF). The SF method uses empirically determined proportions between the concentrations of DTM radionuclides and the concentrations of gamma emitters measurable by gamma spectrometry of waste packages, called key nuclides (KN).

Determining usable SF requires sampling and analysis of filters from several waste generation campaigns for the results to have statistical significance. Even when the waste composition is reasonably constant among the various generation campaigns, the examination of the uniformity of the composition along the time is required.

Besides the laborious and time-consuming preparation of samples and the extensive work to analyze several radionuclides, there remains the issue of the representativeness of a sample, a problem linked to the intra-campaign homogeneity of the waste. If it can be observed that DTM and KN are both distributed evenly in the filters of each waste batch, fewer samples are necessary, reducing laboratory work and costs.

This paper describes a set of methods for the radiochemical characterization of the filters used in the IEA-R1 reactor water cooling system and a study of the activity distribution along the filters by radiochemical analysis, which had not been previously investigated, considering gamma-emitting nuclides concentrations in different sections of the material.

Theory

The literature presents several studies on sequential radiochemical separation methods for the determination of the isotopes of U, Np, Pu, Am, and Cm, a particular group of DTM, in matrices such as soil [7–9], water [10, 11], soil and/or sediment [12–14], sediment and fish [15], soil and vegetation [16], food [17], liquid radioactive waste (sludge, evaporator bottoms) and high level/solid wastes [18–22], evaporator concentrate and/or spent ion exchange resin [23–27], air filter and peat [28], and multiple matrices [19, 29]. These studies employed various techniques for determination of the chemical yields in the radiochemical separation of the analytes before measurements by alpha or gamma-spectrometry, inductively coupled plasma mass spectrometry (ICP-MS), direct current plasma spectrometry (DCP), laser fluorimetry, X-ray spectrometry and liquid scintillation counting (LSC).

In the 1990s, Horwitz et al. [30, 31] developed separation processes using various organic extractive agents, which were later commercially available from Eichrom Technologies, LLC, in the form of chromatographic resins [32]. These materials consist of polymeric support impregnated with extractive agents, the diamyl, amylphosphonate (DAAP), in the case of the UTEVA resin for U, Th, Np, Pu separation, and the *N*-octylphenyl, *N*-di-isobutyl carbamoylphosphine oxide (CMPO) in the case of the TRU resin for Th, U, Pu, Am, Cm, Fe. The first is dependent on the nitrate concentration in the sample, necessary for the formation of complexes with the actinides. The second is dissolved in tri-n-butyl phosphate (TBP) and complexes the actinide elements and extracts them from certain aqueous solutions [33]. For Sr, there is also Eichrom's Sr Resin which contains 4,4′(5′)-di-t-butylcyclohexano 18-crown-6 (crown ether) in 1-octanol on inert polymeric support [34].

Table 1 shows details of the different investigations that are reported in the literature, in which radiochemical methods were applied to measure radionuclides in radioactive waste and other matrices.

Experimental

Materials and equipment

Analytical grade reagents (Merk, Germany) and certified calibrated radiation sources were used in the radiochemical analyzes. All the standards were supplied by the US National Institute of Standards and Technology, NIST. The UTEVA, TRU, Sr, and Ni resins were used for chromatographic extractions and purchased as pre-packed columns, containing 2 mL each, with particle sizes from 100 to 150 µm (Eichrom Technologies Inc., USA). Two strong basic anion exchange resins (1) Dowex 1×2 chloride form, 50–100 mesh (Sigma-Aldrich Inc., USA) packed in 130 mm length and 10 mm diameter glass columns; (2) Dowex 1×8 chloride form, 100–200 mesh (Sigma-Aldrich Inc., USA) packed in 200 mm length and 8 mm diameter glass columns, were also used.

The alpha-emitters were measured by an Alpha Analyst Integrated Alpha Spectrometer (Canberra Industries, USA). This system is constituted by surface barrier semiconductor detectors—passivated implanted planar silicon (PIPS), with the following characteristics: 450 mm^2 active detection area, 20 keV full width at half maximum resolution

Table 1 Radioanalytical methods employed in the analyses of various elements and the chemical yields obtained

Matrix	Analytes	Separation method	Measurement method	Chemical yield (%)	References
Riverine water	Th, Np, U, Pu, Am, and Sr	Chromatographic extraction resins: TEVA (Pu, Th, Np), TRU (U, Am, and Cm) and SR (Sr)	ICP-MS (Pu, Th, Np, U, Am, and Cm), and gas proportional counter (Sr)	Th, Np, U, Pu, Am, and Sr were 93, 81, 84, 80, 80, and 81, respectively	[10]
Liquid high-level nuclear waste	Pu, Np, U, Th, Sr, and Am	Chromatographic extraction resins: TRU (Am and Pu), UTEVA (U), TEVA (Th and Np) and SR (Sr)	Alpha spectrometry for Np, Am, and Pu; ICP-MS for U; DCP for Th; and LSC for Sr	97 (Pu), 97 (Np), 101 (U), 106 (Th), 103 (Sr) and 96 (Am)	[30]
Environmental samples and air filters	Pu	Anion exchange resin	Alpha (^{238}Pu, $^{239+240}$Pu, and ^{242}Pu) spectrometry and liquid scintillation (^{241}Pu)	60–90	[35]
Soil	Pu	Anion exchange resin-AG 1×4	Gamma spectrometry (^{241}Am), alpha spectrometry (^{238}Pu, $^{239+240}$Pu, and ^{242}Pu) and LSC (^{241}Pu)	>70	[8]
Evaporator bottoms	Pu, Am, and U	Anion exchange resin Dowex 1×8 (Pu, U) and chromatographic extraction resin TRU (Am)	Alpha spectrometry	61–97	[27]
Radioactive waste	^{90}Sr	Chromatographic extraction resin: Sr	LSC	81.7, 64.6, and 60	[36]
Concrete	^{63}Ni	Anion exchange resins (Dowex 2×8) and chromatographic extraction resin (Ni)	Atomic absorption spectrometry with graphite furnace and LSC	49–71	[37]
Ion-exchange resin and activated charcoal	^{90}Sr, ^{237}Np, ^{241}Am, ^{244}Cm, ^{60}Co, ^{137}Cs, U and Pu isotopes	Anion exchange resin Dowex 1×8 (Pu/Np), UTEVA (U), TRU (Am/Cm) and Sr (^{90}Sr) chromatographic resins	Gamma spectrometry (^{60}Co and ^{137}Cs), alpha spectrometry (Pu, Np, U, Am, and Cm) and LSC (^{90}Sr and ^{241}Pu)	60–95 (Pu/Np), 75–99 (U), 45–85 (Am/Cm), and 62–85 (Sr)	[3]
Ion exchange resin and activated charcoal	^{59}Ni and ^{63}Ni	Anion exchange resin Dowex 1×4 and chromatographic extraction resin with dimethylglyoxime (DMG)	X-ray spectrometry and LSC	40–94 (resins), 42–97 (coal)	[38]
Ion exchange resin and activated charcoal	26 Radionuclides	Combustion, co-precipitation, chromatographic extraction resin and ion exchange	Alpha spectrometry, LSC, gamma and/or X-ray spectrometry	64–100, depending on the radio-nuclide	[39]

(FWHM), counting efficiency of 17–19% (source-detector distance: 0.5 cm) and calibrated for energies ranging from 3 to 10 MeV. A certified standard source (NIST, Gaithersburg) with electrodeposited ^{234}U (1.301 Bq), ^{238}U (1.317 Bq), ^{239}Pu (1.573 Bq), and ^{241}Am (1.695 Bq) was used to calibrate the system. Genie™ 2000 software (Canberra Industries, USA) was used for data acquisition and analysis. Counting time was 2×10^5 s for each sample.

Beta-emitters were measured with an automatic HIDEX OY model 300 SL liquid scintillation counter, using an automatic triple to double coincidence ratio (TDCR) to correct quenching with an energy discriminator. This discriminator separates alpha and beta for simultaneous counting. Data acquisition and processing were performed by MikroWin Hidex 2000 software, and counting time varied from 3600 to 18,000 s depending on the radionuclide.

The activities of the gamma-emitting radionuclides were performed by gamma-ray spectrometry, employing high purity germanium (HPGe) detector, GX 2518 model (Canberra Industries, USA), with 1.8 keV (FWHM) resolution and 25% relative efficiency for the 1332 keV gamma-ray of ^{60}Co. This system is attached to a multichannel analyzer with 8186 channels and a computer. Genie™ 2000 software (Canberra Industries, USA) was also used for data acquisition and analysis. Counting time was 35,000 s for each sample.

Sample preparation and dissolution of spent filter cartridges

The spent filter cartridges analyzed were stored in the SEG-RR's storage facility, inside 100 L drums. The filters were expected to exhibit a variety of the radioisotopic composition, not only due to the different radioactive decay times but also to variations that occurred during reactor operating conditions. These variations include changes in the operating regime and the thermal power of the reactor, defects in fuel cladding, maintenance of the facility, etc. [40].

Fifteen filters were randomly selected and taken to the laboratory and five thin slices of each one of five filters out of that group were removed as shown in Fig. 1.

Some filter slices were initially measured directly on the gamma spectrometer as a first prospection to identify which gamma-emitting radionuclides were present in the filters. The isotopes ^{60}Co, ^{108m}Ag and ^{110m}Ag were detected. Therefore, the three isotopes ^{60}Co, ^{108m}Ag, and ^{110m}Ag were selected as KN for determination by gamma-ray spectrometry, and the isotopes ^{63}Ni, ^{90}Sr, ^{234,235,248}U, ^{238,239,240}Pu, ^{241}Am, and ^{242,243,244}Cm were selected as radiologically significant and representative DTMs for determination by radiochemical methods.

The difficulty in preparing a calibration source with the same geometry of the filter slices impeded the direct
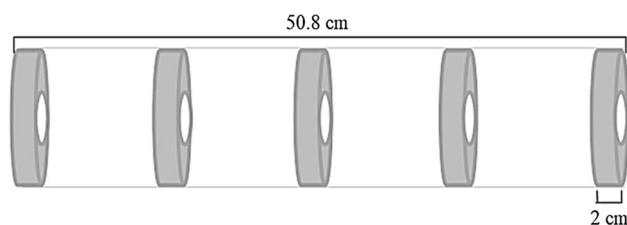

50.8 cm

2 cm

Fig. 1 The scheme adopted in the collection of samples from the cartridge filters

determination of the activity of each sample slice by the gamma spectrometry. Instead, after sampling, each filter slice was cut in half, soaked in alcohol and burnt in a porcelain capsule. After burning, the material was calcined in an oven for 24 h at 350 °C to eliminate any remaining organic compound. For the remaining ten filters, only one slice was taken for radiochemical analysis.

The calcined samples were transferred to a 250 mL Teflon beaker and attacked three times with 20 mL of aqua regia. Between each addition, the samples were heated on a hot plate at 250 °C to dryness. This procedure was repeated with 10 mL of $HClO_4$ 69–72% and 10 mL of 65% HNO_3. Finally, 3 portions of 2 mL of 65% HNO_3, 3 drops of 30% H_2O_2 and 2 mL of deionized water were added for the elimination of aqua regia, HF and $HClO_4$. The samples were dried and cooled to room temperature, the salts were solubilized with approximately 20 mL of 8 mol L^{-1} HNO_3.

After dissolution, the samples were transferred to volumetric balloons and the 100 mL volumes were completed with 8 mol L^{-1} HNO_3 solutions to form the stock solutions for each filter sample. After homogenization, an aliquot of 10 mL was taken from each balloon, transferred to a glass vial with 20 mL capacity, which was sealed and measured in the gamma-ray spectrometer, in the same geometry of previously measured standard solutions, to determine the activity concentrations of ^{60}Co, ^{108m}Ag and ^{110m}Ag.

Sequential determination of U, Pu, Am, and Cm

The sequential analysis involves the use of ion-exchange and chromatographic resins, through which nitric solutions are percolated, and for which the affinity and distribution coefficients depend on the oxidation state of the elements. Those that form nitrate-complexes are retained in the anion exchanger. Therefore, Th(IV), Pa(IV), Np(IV), Pu(IV), Pd(IV), Pd(II), Au(III), Re(VII) and Tc(VII) are easily separated from elements in the forms such as Al(III), Fe(II and III), alkali metals, alkaline earths, lanthanides and trivalent actinides [41, 42].

In concentrated nitric acid (6–10 mol L^{-1}), Pu and Np are found as the complexes $[Pu(NO_3)_6]^{-2}$ and $[Np(NO_3)_6]^{-2}$, which are adsorbed by the anionic resin.

However, the complex $[Pu(NO_3)_5]^{-2}$ may be also present and only partially adsorbed by the anionic resin. To avoid this problem, prior to percolation, the oxidation state of Pu must be adjusted. This involves reducing all valencies of this metal to the trivalent state using nitric acid containing 0.3 grams of sodium nitrite to reduce Pu to Pu(IV) [43].

To do that, 20 mL aliquots withdrawn from the stock solutions were added to 250 mL beakers. The tracers ^{232}U (0.06 Bq), ^{242}Pu (0.07 Bq), and ^{243}Am (0.05 Bq) were then added to monitor the chemical yields of the process. The ^{243}Am tracer was employed for both ^{241}Am and the curium isotopes since americium and curium present the same chemical properties. The oxidation state of Pu(III) was adjusted to (IV) with about 0.30 g of sodium nitrite to enable its retention in the Dowex resin. The aliquots were percolated in columns containing 1×2 Dowex resin, preconditioned with 50 mL 8 mol L^{-1} HNO_3 at 1.5 mL min^{-1}. After percolation, 3×40 mL of 8 mol L^{-1} HNO_3 were added at the same flow rate. The entire effluents were collected, for further analyses of U, Am, and Cm. Three batches of 40 mL 9 mol L^{-1} HCl were added to eliminate possible interferents and to exchange the acidic resin medium. At this stage, flow control was unnecessary and the effluents were discarded. The Pu trapped in the resin columns was oxidized to (IV) form with 0.30 g of hydroxylamine hydrochloride PA, prior to its elution with 3×30 mL 0.5 mol L^{-1} HCl at 1.5 mL min^{-1}. The Pu eluates were dried in heating plates, dissolved with 10 mL 1 mol L^{-1} HNO_3, and transferred to 25 mL volumetric flasks, completed with deionized water.

The effluents containing U, Am, and Cm were separately heated to dryness and then diluted with 20 mL 3 mol L^{-1} HNO_3. About 0.1 g of ascorbic acid was added to reduce possible interferences of Fe(III), by reducing it to Fe(II). The presence of Fe(III) impairs americium retention on the chromatographic extraction column of TRU resin.

An apparatus was assembled containing the UTEVA and TRU chromatographic extraction columns in series, with one column under the other. The solutions were percolated in the columns preconditioned with 20 mL 3 mol L^{-1} HNO_3. After the percolation process, 2×20 mL 3 mol L^{-1} HNO_3 were added to the columns and all the effluents were discarded.

The columns were separated and Am and Cm were eluted from the TRU resin and U from the UTEVA resin. The elution of Am and Cm was carried out by the addition of 5 mL 9 mol L^{-1} HCl and 30 mL 4 mol L^{-1} HCl. For the elution of U, the UTEVA resin was preconditioned with 10 mL 9 mol L^{-1} HCl and the effluent was discarded. The U was then eluted with 2×15 mL 0.01 mol L^{-1} HCl without the need for flow control. The eluates of U, Pu, Am, and Cm were reserved for the preparation of the alpha sources by electrodeposition.

Electrodeposition of U, Pu, Am, and Cm

The eluate solutions were dried on a hot plate and then dissolved with 3 drops of 3 mol L^{-1} H_2SO_4 and 3 mL 0.8 mol L^{-1} $(NH_4)_2SO_4$. The samples were transferred to the electrodeposition cells with 5 mL 0.8 mol L^{-1} $(NH_4)_2SO_4$ and the pH adjusted to between 2 and 3 with 28% NH_4OH and 3 mol L^{-1} H_2SO_4, using 3 drops of 0.1% thymol blue as an indicator. The color considered as the turning point was the light salmon. The electrodeposition was conducted in a current of 1.20 A for 90 min, on polished silver plates. After electrodeposition, the plates were rinsed with distilled water and 70% ethyl alcohol solution and dried on a hot plate. The electrodeposited samples were then analyzed on the alpha spectrometer. Figure S1 presents a flowchart of the separation process of the isotopes of U, Pu, Am, and Cm.

Determination of ^{90}Sr

A volume of 20 mL of stock solution (100 mL flask) and 1 mL of 0.1 g L^{-1} $SrCO_3$ carrier solution were added to beakers. The samples were percolated in a chromatographic extraction column (Sr resin), preconditioned with 50 mL 8 mol L^{-1} HNO_3. After percolation of the samples, 3×10 mL 8 mol L^{-1} HNO_3 were added and the effluents were discarded. The Sr retained in the columns was eluted with 3×10 mL 0.05 mol L^{-1} HNO_3 and the eluted fractions were collected.

A mass of 0.3 g of oxalic acid was added to each fraction and heated. The Sr was precipitated hot with 28% NH_4OH and the pH of the solutions was raised to 9.5–10.

The samples were kept standing for 1 h and the precipitates were filtered off with blue strip paper (150 mm, C42, ash content: 0.00012 g) (Unifil, Brazil). The papers containing the precipitate were dried in a preheated oven to 100 °C for 1 h, then placed in vials proper for analysis by liquid scintillation counting and 1 mL 1 mol L^{-1} HNO_3 was added to dissolve the precipitate. The vials were closed, heated slightly on a hot plate and 15 mL of scintillation solution (Ultima Gold AB Packard cocktail) were added thereto. The samples were then analyzed in a liquid scintillation counter. Figure S2 presents the flow diagram of ^{90}Sr separation.

Determination of the ^{63}Ni

For separation and determination of Ni, it was adopted a combination of radiochemical procedures, necessary for the efficient separation of Ni from interfering isotopes of Cs, Sr, and lanthanides [38]. In this context, a sequential procedure was used to determine Ni, based on the initial precipitation with hydroxides followed by anion chromatography to separate Ni–Fe and in chromatographic extraction with columns impregnated with dimethylglyoxime (DMG) for Ni

purification [3, 38]. Although there is no ^{55}Fe in the filters, due to the short half-life of this element and the long storage time of the filters, this procedure was adopted because the presence of stable Fe can interfere in Ni analysis.

In a beaker, it was added 15 mL of the stock solution (100 mL flask) and 2 mL of Merck's standard 1000 mg L^{-1} Ni solution. The pH was adjusted to 9 with NaOH to precipitate Ni(OH)$_2$. After separation by centrifugation, the precipitate was dissolved with 5 mL 9 mol L^{-1} HCl, and percolated on an anion exchange column (Dowex 1×4), preconditioned with 20 mL 9 mol L^{-1} HCl. Note that Ni^{3+} passes through the resin and the Ni isotopes are collected in the effluent. The column was washed with 40 mL 9 mol L^{-1} HCl and the solution further collected. The column was washed again with 30 mL 4 mol L^{-1} HCl eliminating Co^{2+}. This solution was discarded, and the column rewashed with 30 mL 0.5 mol L^{-1} HCl.

The Ni-containing effluent was evaporated, and the salts dissolved with 2 mL 1 mol L^{-1} HCl and 2 mL 1 mol L^{-1} ammonium citrate solution. A pH adjustment was made to 8–9 by the addition of 28% NH$_4$OH. This Ni-containing solution was percolated on a chromatographic extraction column (Ni resin containing polymer support impregnated with DMG), washed with 20 mL of 0.2 mol L^{-1} ammonium citrate solution at pH 8. The generated effluent was discarded. The function of ammonium citrate is to prevent precipitates consisting of metal hydroxides such as Fe, Cr, and Eu from forming in the column, impairing the separation process. The Ni was eluted in the chromatographic extraction column (Ni resin) with 10 mL of 3 mol L^{-1} HNO$_3$, evaporated in two evaporation steps. Afterward, an aliquot of 0.1 mL was pipetted and added to 10 mL with 1% HNO$_3$ for the determination of the Ni chemical yield by ICP-OES.

Finally, 15 mL scintillation solution (Ultima Gold AB Packard cocktail, USA) was added into the solution to determine ^{63}Ni activity by liquid scintillation counting for 3600 s. The detection efficiency of the counter was determined using a ^{63}Ni standard. Figure S3 shows the flow chart of ^{63}Ni separation.

Determination of the homogeneity of the filter

The values of concentration of all gamma-emitting radionuclides were transformed into a standardized value in order to compare the variation of concentrations of all samples of a filter in a single graph. The Z-score transforms each actual value of measured concentration into the number of standard deviations it is far from the mean. The Z-score is calculated as the difference between the observed concentration of activity in each slice and the mean of the five slices, divided by the standard deviation, according to (1):

$$Z = \frac{x - \bar{x}}{\sigma} \tag{1}$$

where x is the measured value of each slice, $\bar{x}$ is the average and σ the standard deviation of the five values.

Results and discussion

Calcination of the samples, dissolution of the ashes and gamma spectrometry of the resulting solution was selected as the method to determine the concentration of gamma emitters in filter samples because it was difficult to produce a calibration source with the same geometry of a filter slice, due to the hydrophobic behavior of the fresh filter material.

The selected gamma-emitting radionuclides have melting points higher than that used in the furnace, so no loss of these radionuclides is expected by evaporation or sublimation. However, preliminary tests were performed by adding radioactive and stable cobalt tracers to the slice of a new unused filter, which was calcined and the chemical recovery factor measured. No detectable variation was observed in relation to the initial quantity of the cobalt tracers. Results obtained by gamma spectrometry and ICP analysis showed that there was no significant variation between the cobalt quantity in the filter before and after the calcination.

A gamma-ray spectrum, obtained with a 35,000 s measurement of the filter sample, is shown in Fig. 2.

Among the gamma-ray-emitting radionuclides present in the filters (^{60}Co, ^{108m}Ag, and ^{110m}Ag) with activity high enough to be observable in the spectrum, only ^{60}Co had been previously selected as a key radionuclide. It is worth noting the absence of ^{137}Cs in the spectrum, since this radionuclide is one of the most frequent and abundant in nuclear reactor waste, and easily detected by gamma spectrometry due to the high-yield photon of 660 keV emitted by its daughter ^{137m}Ba. The most probable explanation for the absence of ^{137}Cs in the filter is the high solubility of cesium compounds, which can make its presence in suspended solids in the reactor
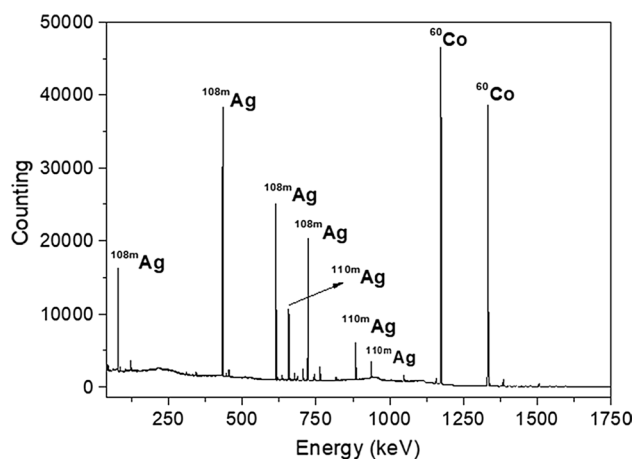

Fig. 2 Gamma spectrum of a filter sample; counting time: 35,000 s

cooling water undetectable by gamma spectrometry. In fact, Taddei et al. [39] detected ^{137}Cs in the other two filters of the IEA-R1 cooling water system, the ion-exchange resin, and the charcoal bed, with the second-highest concentration among all detected radionuclides.

The homogeneity of the distribution of radionuclides in the filters can be evaluated in the graphs of Fig. 3. The graphs represent the Z-score of the measured concentration of the KN in slices of five randomly selected filters. For each radionuclide and each filter, a relative interval (RI) of 30% of the average was calculated above and below the average concentration obtained with the five slices of a filter. According to IAEA [6], all measurement results falling inside the 30% limit is an acceptable criterion of homogeneity for radioactive waste.

No statistical test was used to demonstrate, with any degree of confidence, that the distribution of radionuclide concentrations along each filter is even, but the results, with

the possible exception of filter (a), gives no evidence of a skewed distribution towards the center or the ends of the cylindrical filter.

Mean values of activity in the determinations for the whole filters are listed in Table 2. Figure 4 shows the graph of activity by radionuclide and filter. It is interesting to note that there are roughly three groups of radionuclides according to the order of magnitude of activities. The first and more active is that of the activation products: [60]Co, [63]Ni, [108m]Ag and [110m]Ag. The second is formed by the plutonium isotopes, americium, and [90]Sr. The third group contains the uranium and curium isotopes.

The presented activities are that calculated for each filter at the date the filters were collected from the IEA-R1 facility. Note that for the calculation of scaling factors between KNs and DTMs, the activity must be corrected to the date when the filters were removed from the water purification system of the reactor cooling circuit. As no record of this information
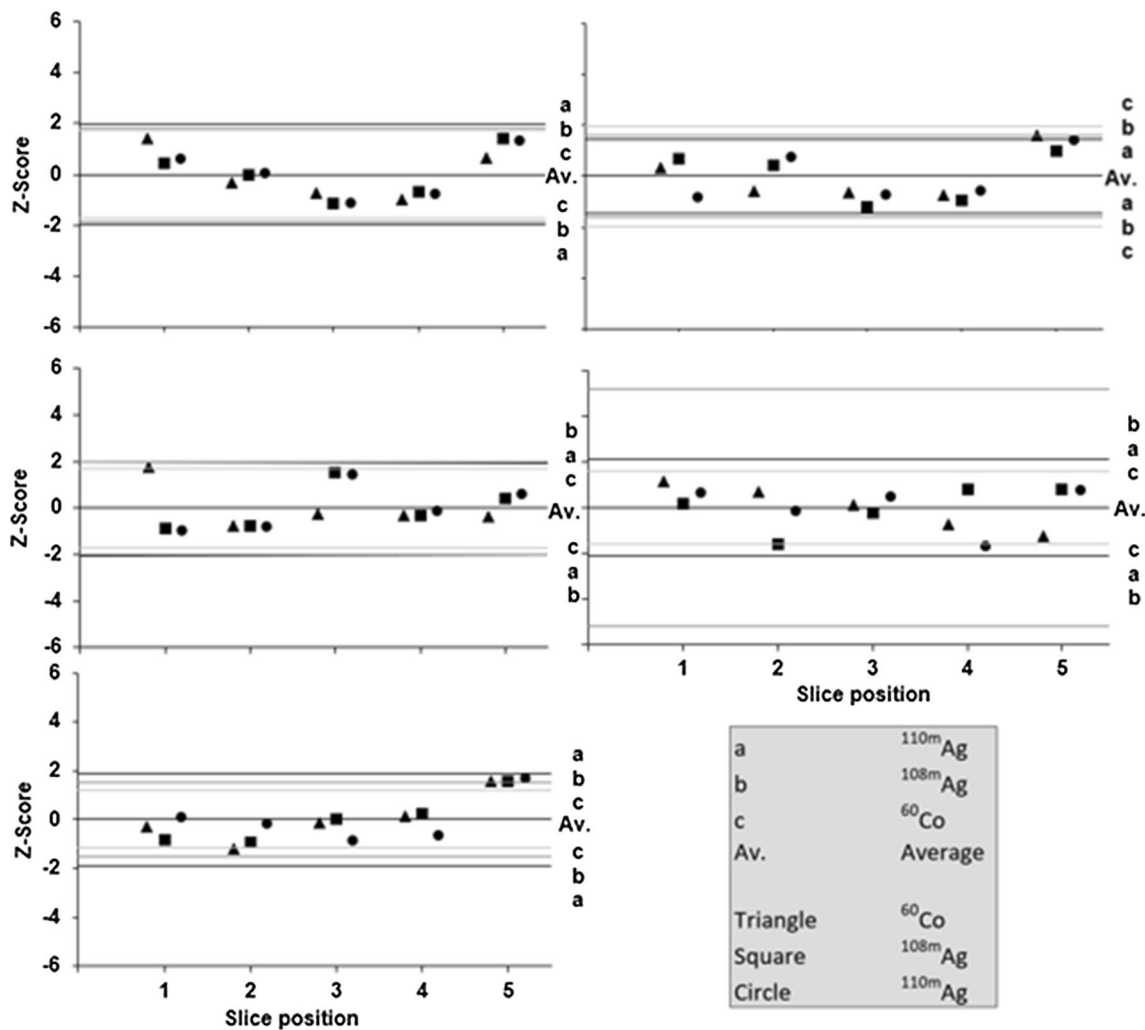

Fig. 3 Evaluation of homogeneity by gamma spectrometry of a sample of five randomly selected filters

Table 2 Calculated activities of the selected radionuclides in whole filters

Filter No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
^{60}Co ($\times 10^5$)	4.68±0.06	16.6±0.21	5.30±0.07	4.84±0.06	6.53±0.08	3.05±0.04	4.19±0.05	7.25±0.09	3.11±0.04	3.52±0.05	4.34±0.06	3.90±0.05	4.10±0.05	4.63±0.06	4.14±0.05
^{65}Ni ($\times 10^4$)	4.01±0.05	11.8±0.12	4.11±0.04	3.14±0.03	5.59±0.06	2.17±0.02	2.73±0.03	3.83±0.04	1.81±0.02	2.63±0.03	3.08±0.04	2.44±0.03	3.38±0.04	3.94±0.03	2.90±0.03
^{90}Sr ($\times 10^2$)	1.80±0.14	5.24±0.43	5.31±0.42	6.61±0.51	5.49±0.44	2.83±0.22	4.93±0.40	2.87±0.22	10.9±0.84	2.71±0.24	42.1±3.51	3.12±0.24	18.5±1.49	4.17±0.33	12.0±0.96
^{108m}Ag ($\times 10^4$)	7.57±0.12	6.57±0.10	10.4±0.16	11.0±0.17	3.28±0.05	5.20±0.08	3.18±0.05	5.02±0.08	5.29±0.08	6.24±0.09	7.29±0.11	5.03±0.08	7.36±0.11	8.99±0.14	8.46±0.13
^{110m}Ag ($\times 10^4$)	4.33±0.06	22.9±0.27	5.58±0.07	5.82±0.07	10.8±0.13	2.45±0.03	8.54±0.10	18.5±0.21	2.42±0.03	4.50±0.06	1.83±0.03	4.02±0.05	3.95±0.05	3.54±0.05	7.34±0.09
^{234}U ($\times 10^{-1}$)	6.69±0.70	10.7±0.93	8.43±0.84	8.58±0.78	6.27±0.63	5.36±0.55	10.6±0.88	9.81±0.82	4.40±0.54	5.13±0.51	4.22±0.48	4.71±0.49	5.73±0.57	7.01±0.65	4.96±0.52
^{235}U ($\times 10^{-3}$)	36.1±17.2	47.5±18.1	51.1±2.33	61.32±19.2	45.7±18.4	21.1±14.6	39.6±16.7	28.7±15.1	<5.42	36.4±11.7	6.06±12.2	<5.42	<5.42	28.6±14.8	13.0±12.7
^{238}U ($\times 10^{-1}$)	2.73±0.41	4.16±0.50	4.94±0.60	3.32±0.43	3.86±0.46	1.84±0.29	3.48±0.42	3.13±0.39	1.63±0.31	1.67±0.26	1.58±0.27	2.21±0.31	1.87±0.29	2.14±0.31	1.61±0.27
^{238}Pu ($\times 10^1$)	2.25±0.13	6.59±0.35	2.29±0.13	1.84±0.11	4.87±0.27	2.39±0.14	5.07±0.31	5.67±0.30	3.57±0.21	3.51±0.20	3.57±0.20	1.41±0.08	1.58±0.10	1.46±0.09	2.25±0.13
$^{239+240}$Pu ($\times 10^2$)	0.98±0.05	2.81±0.15	1.14±0.06	0.80±0.04	1.64±0.09	0.62±0.03	1.02±0.10	2.02±0.10	0.52±0.03	0.96±0.05	0.96±0.05	0.47±0.02	0.73±0.04	0.74±0.04	0.80±0.04
^{241}Am ($\times 10^2$)	0.54±0.03	1.13±0.06	0.65±0.03	0.55±0.03	0.39±0.02	0.65±0.04	0.36±0.03	1.19±0.06	0.46±0.03	0.54±0.03	0.62±0.03	0.43±0.02	0.58±0.03	0.66±0.04	0.41±0.02
^{242}Cm ($\times 10^{-1}$)	1.04±0.28	3.64±0.54	1.74±0.36	1.18±0.29	1.88±0.28	2.13±0.42	5.04±1.30	5.13±0.60	2.05±0.39	1.18±0.31	3.22±0.49	2.80±0.39	3.30±0.60	3.16±0.42	2.78±0.35
$^{243+244}$Cm ($\times 10^{-1}$)	5.48±0.65	20.2±1.58	6.62±0.73	5.17±0.62	12.2±0.88	6.58±0.85	16.1±2.47	27.1±1.92	6.16±0.67	9.15±0.93	9.66±0.93	7.21±0.68	8.31±0.99	12.5±1.00	6.07±0.62

Fig. 4 The calculated activity of the radionuclides determined in filters. Obs.: values outside the scale in the graph are those below determination limits by the methods used in the analyses
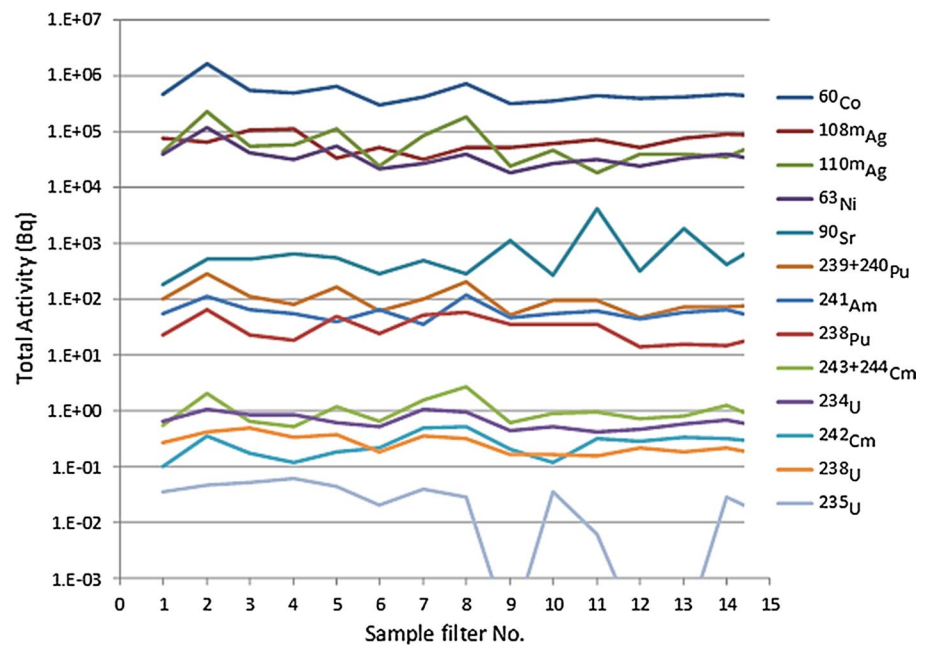
was available, the date of collection of the waste to the waste management facility was used instead. The systematic error incurred is, however small taking into consideration that the decay time of the filters between replacement and transport is negligible as compared with the half-lives of all measured radionuclides, with the possible exception of ^{110m}Ag, which do not affect significantly, however, the results.

In general, the most abundant DTM radionuclide in the three main radioactive waste matrices (cartridge filters, charcoal filter beds, and ion-exchange resin) was ^{63}Ni, an activation product with lower radiological significance.

The isotope ^{90}Sr is usually in the soluble form, which explains the low activity found in the filter samples and, therefore, was retained predominantly by adsorption in activated charcoal or by ion exchange in the ion-exchange resin bed of the water purification system [3].

It is difficult to perform a mass balance of radioactive substances in the reactor waste because of the different operating regimes. While the charcoal beds and ion-exchange resin beds are replaced after several years in service, the cartridge filters are replaced usually six times per year. Consequently, only after the waste characterization program has accumulated results for all waste streams, it will be possible to have a picture of the distribution of radionuclides among the waste matrices.

Conclusions

A radiochemical analysis method was developed for the radioisotope characterization of the cartridge filters used to purify the water of the primary circuit in the IEA-R1 reactor cooling system. These filters have a cylindrical geometry with 7 cm in diameter and 50 cm in length, are made of expanded polypropylene and are used to remove suspended solids from the coolant.

The difficult-to-measure (DTM) radionuclides were determined by a method of radiochemical separation with specific chromatographic resins and subsequent quantification by alpha spectrometry and beta counting. The easily measurable gamma emitters called key nuclides (KN) were determined by gamma spectrometry.

It was a difficult task to establishing a method of complete dissolution of the filters for the radiochemical analyses because the chemical composition of the filters made them insoluble in acids even under heating. The problem was overcome by complete calcination of the samples. It was possible to completely dissolve the filter material, to obtain a clear solution to form the stock solution for analysis.

A set of 15 filters with varying decay times were randomly selected from the stockpile in the waste storage. To reduce the number of samples from each filter and reduce the time and resources required for the radiochemical analyses, the uniformity of the distribution of radionuclides along the cylindrical filters was evaluated by gamma spectrometry. It was expected from the beginning, a homogeneous distribution of radionuclides along the filter, because of the filter holder geometry and the turbulent water flow conditions in the cooling water system. The results confirmed that assumption and supported the decision of taking only one thin slice as an acceptable, representative sample of each filter.

From the results, the correlation between the selected DTM and KN radionuclides was determined and will allow

for the determination of the radioisotopic inventory, or source term, in the routine waste characterization program at IPEN. No ^{137}Cs could be detected in the filter samples, unlike results obtained with other waste streams from the reactor, indicating that all cesium contained in the water is in the dissolved phase and was removed from the cooling water by the charcoal and ion-exchange resin beds by adsorption and ion exchange, respectively.

The radionuclide with the highest average activity per filter is ^{60}Co, of the order of 0.53 MBq, in the sequence ^{63}Ni, ^{108m}Ag, and ^{110m}Ag of the order of 3.84×10^4, 6.72×10^4, 7.10×10^4, respectively. The radionuclides ^{90}Sr, $^{239+240}$Pu, ^{238}Pu, and ^{241}Am presented mean activities of 8.57×10^2, 1.08×10^2, 32.2 and 61.1 Bq, respectively. The activities of isotopes of U and Cm are low, some samples even showing concentrations lower than the minimum detectable activity for ^{235}U. The mean activities of the remaining radionuclides are ^{234}U (6.84×10^{-1} Bq), ^{235}U (3.46×10^{-2} Bq), ^{238}U (2.68×10^{-1} Bq), ^{242}Cm (2.69×10^{-1} Bq) and $^{243+244}$Cm (0.11×10^{-1} Bq).

The average chemical yields for each radionuclide varied from 70 to 97% for ^{63}Ni, 79–96% for U, 62–74% for Pu and Am and 65–83% for Cm isotopes.

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