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A comparative study using liquid scintillation counting and X-ray spectrometry to determine ^{55}Fe in radioactive wastes

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Abstract The radionuclide ^{55}Fe was determined in samples of radioactive wastes from the water cleanup system of the IEA-R1 nuclear research reactor. In order to validate the results, the ^{55}Fe activity concentration was measured in eight waste samples and in six simulated samples containing the most important interfering radionuclides. A simple method was employed to separate and purify ^{55}Fe from other radionuclides present in these samples, combining co-precipitation with ammonium hydroxide and purification with anionic ion-exchange resin, which enables ^{55}Fe to be quantified either by liquid scintillation counting (LSC) or by X-ray spectrometry using a low-energy germanium spectrometer (LEGe). Both measurement methods were used so that the separation and purification process could be confirmed by comparison of spectra with and without the utilization of anionic ion-exchange resin. Activity and interferences were compared in the results obtained from LSC and LEGe measurement methods.

Keywords Research reactors · Radioactive wastes · Difficult to measure radionuclides · Liquid scintillation counting · X-ray spectrometry · Ion-exchange resin

Introduction

The IEA-R1 is a 5 MW pool-type nuclear research reactor moderated and cooled by light water. It is located at the Nuclear and Energy Research Institute (IPEN/CNEN-SP) and used for scientific research as well as to produce radioisotopes [1, 2].

Iron and nickel are important components of stainless steel, a common structural material used in nuclear reactors. This is the main source of ^{55}Fe produced in nuclear reactors by neutron activation of the most abundant stable isotopes of iron and nickel. In the IEA-R1 nuclear research reactor, ^{55}Fe production by neutron activation of nickel also occurs on the cladding of the control rods, which consists of a thin layer of metallic Ni.

The radionuclide ^{55}Fe decays by electron capture to stable ^{55}Mn with emission of low energy X-rays and Auger electrons. Its main properties [3, 4] are summarized in Table 1.

As a consequence of its relatively short half-life and emission of low energy X-rays, ^{55}Fe is not a radiological protection concern in radioactive wastes stored for a long time [4], although it is considered the main origin of activity in fresh radioactive waste from nuclear reactors [5]. Nevertheless, the low energy of the emitted X-rays hinders the direct determination by means of non-destructive gamma-ray spectrometry, which makes ^{55}Fe one of the difficult to measure (DTM) radionuclides present in radioactive waste [6].

In the analysis of radioactive waste from nuclear reactors, the greatest problem is to determine the activity concentrations of beta- or low-energy X-rays emitters due to the interferences of many radionuclides contained in the samples. Thus, a high degree of radiochemical purification is required in order to eliminate such interferences. Several

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Table 1 Properties of the radionuclide ^{55}Fe: half-life $T_{1/2}$, main production nuclear reactions, threshold energy E_{th} of the nuclear reaction, isotopic abundance f of the stable target nucleus, radioactive decay mode (EC – electron capture) and main radiations emitted in the decay (energy E_X and absolute emission intensity I_X of the X-rays emitted; kinetic energy E_A and absolute emission intensity I_A of the Auger electrons emitted) [3, 4]

Radionuclide	$T_{1/2}$ (years)	Main production reactions	E_{th} (MeV)	f (%)	Decay mode	Main radiations emitted			
						E_X (keV)	I_X (%)	E_A (keV)	I_A (%)
^{55}Fe	2.74	^{54}Fe(n,γ)^{55}Fe	–	5.80	EC	5.9	25.0	5.2	60
		^{56}Fe(n,2n)^{55}Fe	11.4	91.70		6.5	3.38		
		^{56}Fe(γ,n)^{55}Fe	11.2						
		^{58}Ni(n,α)^{55}Fe	3.1	68.27					

separation and purification steps involving the use of precipitation, ion chromatography or liquid–liquid extraction methods are required before counting.

Purification of ^{55}Fe in radioactive waste samples is commonly performed by liquid–liquid solvent extraction where $FeCl_3$ is extracted in di-isopropyl ether. However, an alternative is chromatographic extraction using TRU-spec® resins where $Fe(NO_3)_3$ is extracted with CMPO (octylphenyl-*N*,*N*-di-isobutyl carbamoylphosphine oxide) dissolved in TBP (tri-*n*-butyl phosphate). This material is purchased as pre-packed columns from Eichrom Technologies [7–10].

Another method for purification of ^{55}Fe employs a strong alkaline anionic ion-exchange resin in which the separation of metals by differential adsorption of their chlorine complexes is very efficient. This method is based on formation of the $FeCl_4^-$ complex in a strongly acid HCl solution, which will be exchanged later in the resin [5, 11].

This work describes a simple method for purification of ^{55}Fe using co-precipitation and anionic ion-exchange resin in samples of spent ion-exchange resin and activated charcoal beds that were permanently withdrawn from the water cleanup system of the IEA-R1 nuclear research reactor. The overall efficiency of the method was confirmed by means of analysis of the simulated samples added with the main interfering radionuclides and measured by liquid scintillation counting (LSC) and X-ray spectrometry using a low-energy germanium spectrometer (LEGe). Chemical yield of the stable Fe used as carrier and tracer was determined by inductively coupled plasma optical emission spectrometry (ICP-OES). Linear regression and the paired *t* test were employed in order to compare both measurement methods.

Experimental

Materials and equipment

Only analytical grade reagents were used during the analysis performed in the scope of the radiochemical method. Dowex® anionic ion-exchange resin (1 × 4, 50–100 mesh Tyler) was purchased from Sigma-Aldrich Inc.

The ^{55}Fe activity concentration was measured by X-ray spectrometry using a low-energy germanium spectrometer (LEGe, model GL2020R) from Canberra Industries. Genie™ 2000 software was used in order to acquire X-ray spectra, as well as to identify and analyze full-energy peaks. In situ object calibration (ISOCS) and laboratory sourceless object calibration (LabSOCS) software were used in order to perform the efficiency calibration and to discount self-attenuation effects. All mentioned software products are from Camberra Industries. The resolution (FWHM) obtained for the full-energy peak of 5.9 keV was 0.306 keV.

An iron standard solution of 10 g L^{-1}, purchased from Sigma-Aldrich Chemie GmbH, was used in order to add the stable Fe employed as carrier and tracer. Chemical yield of stable Fe was measured by ICP-OES using a Liberty RL Sequential Spectrometer from Varian Inc.

The ^{55}Fe activity concentration was measured by LSC with an automatic HIDEX liquid scintillation counter (model 300SL), using triple to double coincidence ratio (TDCR) and the Ultima-Gold AB™ scintillation cocktail from Perkin Elmer. A ^{55}Fe standard solution (number 104 L 10), provided by NPL-UK and calibrated by the National Laboratory of Metrology of the Ionizing Radiations (LNMRI, Brazil), was used as reference material. MikroWin Hidex 2000 software (from HIDEX, Finland) was used for data acquisition and processing.

Dissolution of radioactive waste samples

Approximately 1–2 g of each sample of spent ion-exchange resin was transferred to PTFE beakers and dissolved with successive additions of nitric acid, hydrogen peroxide and perchloric acid. Temperature was maintained between 250 and 300 °C using an electric plate. The samples were always dried after each addition in the following sequence: (a) twice with 10 mL of HNO_3 + 5 mL of H_2O_2; (b) once with 10 mL of HNO_3 + 5 mL of

$HClO_4$; (c) once with 10 mL of HNO_3 + 5 mL of H_2O_2. After the last addition and drying procedure, the remaining salts were dissolved with 8 mol L^{-1} of HNO_3 and the sample completed with 8 mol L^{-1} of HNO_3 in a volumetric flask of 100 mL, forming a stock solution from which the aliquots were taken for the analyses.

The activated charcoal samples were transferred to porcelain crucibles, weighted (mass of approximately 2 g for each sample) and calcined progressively in a muffle furnace at a rate of 0.8 °C min^{-1} until reaching 450 °C. This temperature was maintained for 24 h to eliminate from the charcoal sample as much organic matter as possible in order to facilitate the dissolution process. The dissolution process is similar to that used for samples of spent ion-exchange resin, except that $HClO_4$ has been replaced by the same quantity of concentrated HF because of the higher silica content of the samples. Also in this case, after the last addition and drying cycle, the remaining salts were dissolved and the sample completed with 8 mol L^{-1} of HNO_3 in a volumetric flask of 100 mL, forming another stock solution from which the aliquots were taken for the analyses.

Separation procedures

Before each measurement, a 10 mL aliquot of the stock solution was transferred to a 200 mL beaker to which 4 mL of stable Fe carrier was added from a 10 g L^{-1} standard solution. The resultant solution was stirred during dilution to 30–40 mL with deionized water, its pH was elevated to 8–9 using concentrated ammonium hydroxide and precipitation of $Fe(OH)_3$ occurred. The solution was allowed to stand undisturbed for 4 h until the precipitate settled. Afterwards, most of the clear solution was carefully discarded or reserved if determination of ^{63}Ni was required.

The $Fe(OH)_3$ precipitate was carefully filtered in vacuum. The filter funnel assembly was on the filter rig. A 47 mm diameter and 0.45 μm porosity cellulose acetate filter from Sartorius Stedim Biotech GmbH, Germany, was used. The funnel was rinsed with a 1 % ammonium solution and the filter was transferred to a beaker in which the precipitate was totally dissolved with 10 mL of 9 mol L^{-1} HCl. Then, the filter was removed from the beaker using tweezers and rinsed with 10 mL of 9 mol L^{-1} HCl employing a pipette.

The solution was percolated through a column with Dowex® anionic ion-exchange resin (1 × 4, 50–100 mesh Tyler) 10 cm long and 0.8 cm in diameter, previously conditioned with 9 mol L^{-1} HCl. This column was washed with 20 mL of 9 mol L^{-1} HCl, followed by three equal portions of 10 mL of 4 mol L^{-1} HCl each, in order to remove ^{60}Co, ^{137}Cs and other interfering radionuclides when the effluent is discarded. Thereafter, Fe was eluted with 30 mL of 0.5 mol L^{-1} HCl and the effluent was collected in a 100 mL beaker where precipitation was carried out again using concentrated ammonium hydroxide with the pH in the range 8–9.

As soon as the precipitate settled completely, the supernatant was carefully removed and the pulp was filtered in vacuum. The filter funnel assembly was on the filter rig. A 47 mm diameter and 0.45 μm porosity cellulose acetate filter, from Sartorius Stedim Biotech GmbH, was used. The funnel was rinsed with a 1 % ammonium solution. The vacuum was disconnected and the filter was removed. The filter was placed in the external side of a Petri dish using tweezers carefully in order to achieve a precise centering and dried under a heat lamp during 4 h. All edges of the filter were secured so that it remained on a support covered by a thin PVC film.

This procedure gave the precipitate a flat surface. It was placed in a counting support and the ^{55}Fe activity concentration was determined by X-ray spectrometry measuring the full-energy peak of 5.9 keV for 18,000 s. Efficiency calibration was performed using the ISOCS and LabSOCS software from Canberra Industries with a ^{55}Fe standard precipitated in the same geometry of the sample. Because of the low energy of the X-rays being measured, the use of a ^{55}Fe standard was necessary in order to discount the high self-attenuation of the sample and the attenuation caused by the thin PVC film.

After the ^{55}Fe activity concentration was determined, the filter containing the precipitate was removed from the support and placed in a 100 mL glass beaker with 20 mL of 0.5 mol L^{-1} HCl. The precipitate was dissolved and the filter was removed from the beaker with a pair of tweezers. The solution was evaporated and the remaining salts were dissolved with 2 mL of 1 mol L^{-1} H_3PO_4 [10]. An aliquot of 0.1 mL was placed in a 25 mL volumetric flask and diluted with 1:1 HNO_3 to determine the chemical yield of stable Fe by ICP-OES. Finally, the rest of the solution was mixed with 15 mL of the Ultima-Gold AB™ scintillation cocktail and the ^{55}Fe activity concentration was determined once again, but this time by LSC in measurement of 1,800 s [5].

All steps of the ^{55}Fe purification and determination process are shown in Fig. 1 using a flow diagram.

Results and discussion

In order to evaluate the purification process described in the previous section, the activity concentration of ^{55}Fe was determined by both LSC and X-ray spectrometry in two samples of spent activated charcoal and six samples of spent ion-exchange resin. Analyses were also carried out on three ^{55}Fe standard solutions with different activities and in three ^{55}Fe standard solutions to which different activities of ^{60}Co and ^{137}Cs—the most important interfering radionuclides

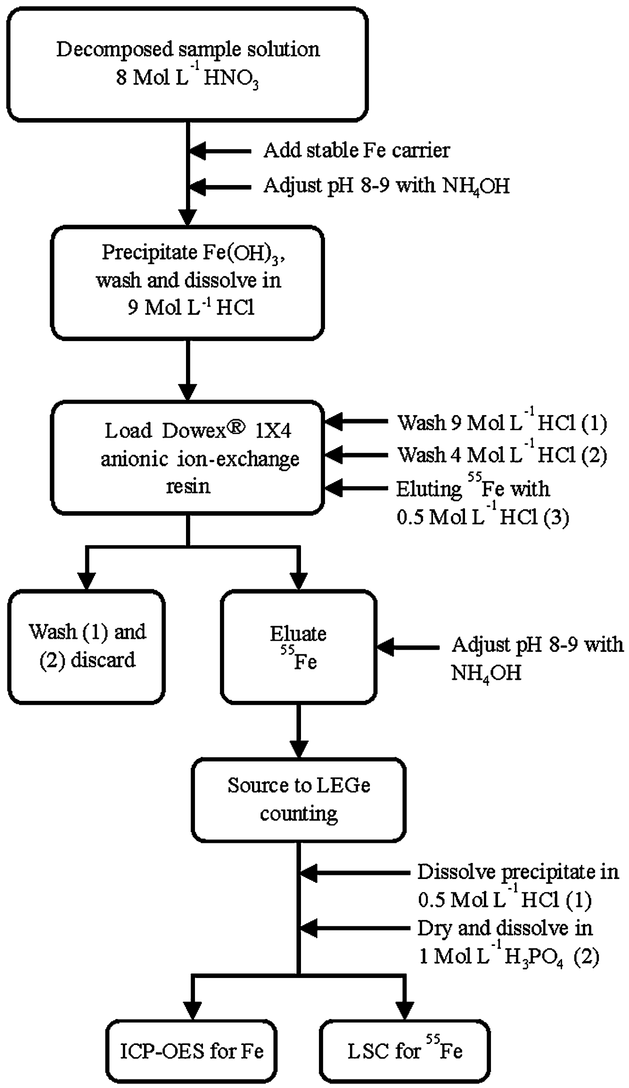

Fig. 1 Flow diagram of the radiochemical process required for purification and determination of ^{55}Fe

in these waste matrixes—were added. Samples obtained from solutions to which ^{60}Co and ^{137}Cs had been added were called simulated samples.

The average efficiency for measurements by LSC using a ^{55}Fe standard of 230 Bq, in the channel range between 10 and 200 with a duration of 1,800 s, was 42 % and, as a consequence, the calculated detection limit [5, 12] for a sample mass of 0.1 g and the same counting time amounted to 0.021 Bq g^{-1}.

Regarding the X-ray spectrometry measurements, most relevant parameters were an efficiency of 9.72 % and a self-attenuation correction of 0.526, both calculated by ISOCS and LabSOCS software that took into account information about geometrical configuration of the system sample—LEGe detector, chemical composition of the sample and linear attenuation coefficients for the photon energy of 5.9 keV. The average counting time was 18,000 s and the ^{55}Fe calculated detection limit [5, 12] for a sample mass of 0.9 g was 0.5 Bq g^{-1}.

Table 2 ^{55}Fe activity concentration results obtained by liquid scintillation counting and X-ray spectrometry for all samples, along with the respective Fe chemical yield determined by ICP-OES

Sample	Liquid scintillation counting (Bq g^{-1})	X-ray spectrometry (Bq g^{-1})	Chemical yield (%)
CA-01	3.47 ± 0.53	2.68 ± 0.70	69
CA-21	2.83 ± 0.38	1.22 ± 0.70	99
RTI-16	4.74 ± 0.67	4.30 ± 0.80	88
RTI-10	9.02 ± 1.19	7.33 ± 1.21	87
RTI-30	4.34 ± 0.43	5.18 ± 0.89	88
RTI-12	0.06 ± 0.005	< 0.30	84
RTI-40	3.04 ± 0.50	2.70 ± 1.20	88
RTI-28	2.06 ± 0.39	2.02 ± 0.35	90
S1 (7.81 Bq)[a]	7.98 ± 0.82	7.77 ± 0.32	76
S2 (8.82 Bq)[a]	8.68 ± 0.73	8.97 ± 1.20	74
S3 (10.50 Bq)[a]	10.30 ± 1.49	10.30 ± 1.20	64
S4 (7.24 Bq)[b]	7.10 ± 0.72	7.06 ± 1.03	77
S5 (8.36 Bq)[b]	8.17 ± 0.83	8.26 ± 1.08	69
S6 (9.99 Bq)[b]	10.45 ± 1.31	10.26 ± 1.42	73

[a] Added activity of the ^{55}Fe standard solution

[b] Added activity of the ^{55}Fe standard solution to simulated samples with ^{137}Cs and ^{60} Co

In order to evaluate the efficiency of the purification process, three simulated samples (S4, S5 and S6) were prepared as previously explained, using ^{55}Fe standard solutions with activities shown on Table 2, along with the following activities concerning the most important interfering radionuclides: sample S4 = 127 Bq of ^{137}Cs and 64 Bq of ^{60}Co; sample S5 = 80 Bq of ^{137}Cs and 38 Bq of ^{60}Co; sample S6 = 47 Bq of ^{137}Cs and 26 Bq of ^{60}Co.

Table 2 shows a summary of all ^{55}Fe activity concentration results obtained by LSC and X-ray spectrometry for the radioactive wastes samples, the ^{55}Fe standard solutions samples and the simulated samples, as well as the Fe chemical yield determined by ICP-OES.

Typical photon spectra obtained from measurements carried out on radioactive wastes samples are shown in Fig. 2. The spectrum from a sample prepared only by means of precipitation during the purification process (Fig. 2a) shows an enhanced baseline due to Compton scattering of higher energy photons emitted by interfering radionuclides. Such phenomenon partially obscures the full-energy peak of 5.9 keV from ^{55}Fe and therefore subtracts counts from the X-ray spectrometry measurements [8]. A much clearer spectrum (Fig. 2b) is obtained for the same sample in which, besides precipitation, an anionic ion-exchange resin is employed in the purification process.

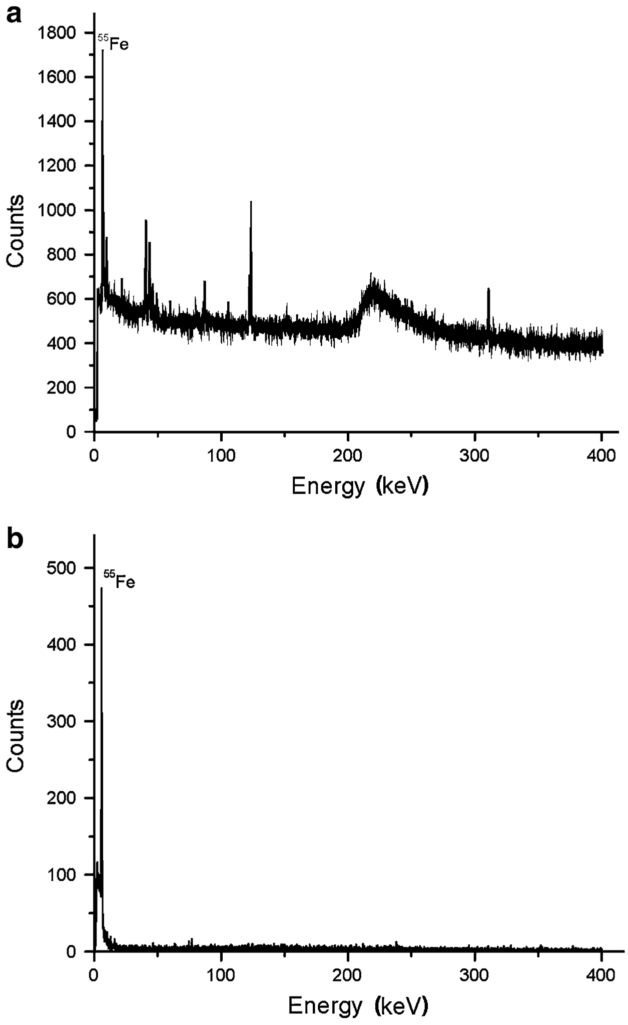

Fig. 2 Photon spectra obtained from measurements of samples **a** with and **b** without interfering radionuclides

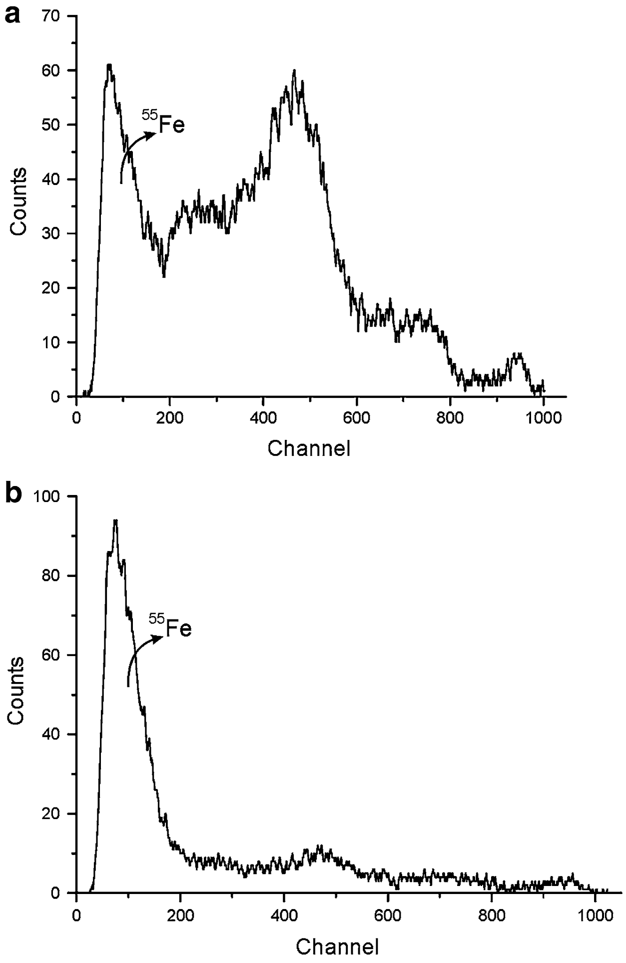

Fig. 3 Beta spectra obtained from measurements of samples **a** with and **b** without interfering radionuclides

These samples were dissolved and measured by LSC and their beta spectra are shown in Fig. 3. Similar to the case of X-ray spectrometry measurements, the presence of interfering radionuclides (Fig. 3a) does not permit a good resolution even when restraining the counting channels. If there is more than one interfering beta-emitter radionuclide in the sample, the identification of radionuclides based on continuous beta spectra becomes difficult, since the overlap of characteristic spectra add counts to the measurements. However, a beta spectrum with good resolution (Fig. 3b) is obtained employing an anionic ion-exchange resin in order to eliminate the interfering radionuclides.

During the early stages of the purification process, not only Fe^{+3}, but also Al^{+3}, Cr^{+3}, Co^{+2}, Cs^{+}, Sr^{+2}, Ba^{+2}, Zn^{+2}, Eu^{+3} and Cu^{+2} are precipitated using concentrated ammonium hydroxide. Different behavior is seen in the case of Ni^{+2}, which is also present but does not precipitate in an ammonia solution, since it forms the complex ion $[Ni(NH_3)_4]^{+2}$, although experimental results show that approximately 20 % of Ni^{+2} is co-precipitated along with $Fe(OH)_3$ [5].

A more efficient method employed to separate Fe from other elements such as Ni, Mn, Cu, Zn and Co consists of restricting the amount of ammonium hydroxide used in the precipitation to a minimum [11]. If Ni is carried along in the beginning of the precipitation, it will be removed later by the anionic ion-exchange resin since it does not form anionic complexes at any hydrochloric acid concentration and therefore is not adsorbed from 9 mol L^{-1} hydrochloric acid in the ion-exchange column. The ions Co^{+2}, Cs^{+}, Sr^{+2}, Ba^{+2}, Zn^{+2}, Eu^{+3} and Cu^{+2} are only weakly adsorbed from 4 mol L^{-1} hydrochloric acid and can be eluted from the ion-exchange column with acid at this concentration, which does not eluted Fe^{+3}. However, Fe can be desorbed with 0.5 mol L^{-1} hydrochloric acid [5, 11, 13].

The methods employed in this work to measure the ^{55}Fe activity concentration in radioactive wastes samples can be compared by applying a paired *t* test [14]. This test shows

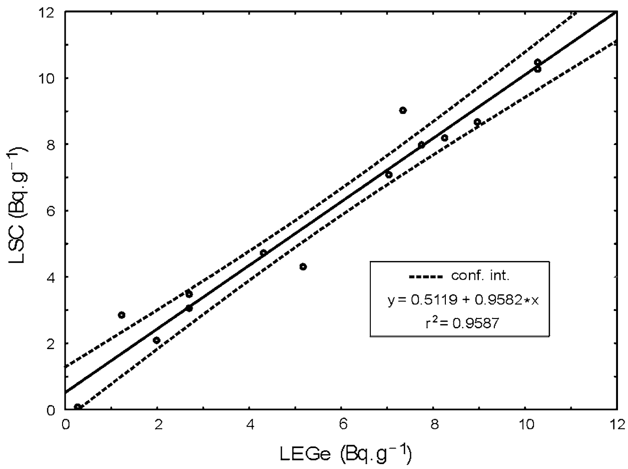

Fig. 4 Scatter plot of the data set of ^{55}Fe activity concentration for all measured samples, comparing the results obtained by liquid scintillation counting (LSC) and X-ray spectrometry using a low-energy germanium spectrometer (LEGe)

with a statistical probability of approximately 96 % that both methods used for purification lead to the same results, since the Student's *t*-criteria 0.157 is considerably smaller than the critical value 1.771. The scatter plot of the data set of ^{55}Fe activity concentration, shown in Fig. 4, exhibits a straight line regression with good correlation between the results obtained by LSC and X-ray spectrometry.

Conclusion

The separation and purification method, employed in this work to determine the ^{55}Fe activity concentration in samples of radioactive wastes from the IEA-R1 nuclear research reactor, was tested by comparing LSC and X-ray spectrometry (LEGe) measurements. This method combines co-precipitation using ammonium hydroxide and purification using anionic ion-exchange resin in order to separate ^{55}Fe from other radionuclides.

High chemical yield of stable Fe was obtained by ICP-OES for this method. Most results of the ^{55}Fe activity concentration obtained for the same sample by LSC and X-ray spectrometry showed good agreement within the experimental uncertainties.

Measurements of the ^{55}Fe activity concentration by LSC have a lower detection limit, but are very susceptible even at low concentrations of interfering radionuclides that may be carried along during the purification process. As a consequence, overestimated results can be obtained due to the difficulty of separating radionuclides based on their continuous beta spectra.

Measurements of the ^{55}Fe activity concentration by X-ray spectrometry, in turn, depend markedly on geometrical parameters and chemical composition of the precipitate sample, which affect the self-attenuation correction and therefore the final result. Moreover, in case of failure in the separation process, the presence of ^{137}Cs and ^{60}Co causes an increase of the baseline due to Compton scattering of higher energy photons that they emit. Consequently, the full-energy peak of 5.9 keV from ^{55}Fe can be partially obscured and the final result underestimated [8].

The use of anionic ion-exchange resin columns is advantageous because they can be recovered, are easily available in chemical analyses laboratories and produce a small volume of waste during the process.

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