

APPLICATION OF LSC FOR THE DETERMINATION OF SOME RADIONUCLIDES IN WASTE MATRICES FROM THE IGNALINA NPP

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ABSTRACT. Liquid scintillation counting (LSC) with a Quantulus™ (Wallac) was used to determine ⁵⁵Fe, ⁶³Ni, ⁹⁰Sr, ¹²⁹I, and ²⁴¹Pu in waste matrices from the Ignalina nuclear power plant (NPP) in Lithuania. Actual radioactive waste samples were destroyed by different techniques according to the character of the matrix. After digestion, the concentrations of existing stable Fe, Ni, and Sr were measured in the original sample using an atomic absorption spectrometer (AAS) with a graphite atomizer (standard deviation 5–10%). A modified combined radiochemical separation procedure was applied for simultaneously determining ⁶³Ni, ⁵⁵Fe, and ⁹⁰Sr from a single sample aliquot. The effective analytical separation of these isotopes from other traces found in radioactive waste was achieved using the following methods. The basic procedure for Fe and Ni analysis consisted of ferric hydroxide coprecipitation, anion-exchange separation of Fe, and extraction chromatographic separation of Ni on the NiSpec column. Separation of Sr was based on the extraction chromatographic procedure on a SrSpec (Eichrom Technologies, Inc.) column developed by Horwitz et al. (1991). An alkaline leaching method for analyzing ¹²⁹I in solid matrix waste samples or an ion-exchange chromatography method for analyzing this radionuclide in water were combined with purification by extraction into chloroform and back-extraction into the aqueous phase. ²⁴¹Pu was determined after purification by liquid-liquid extraction of dissolved material electrodeposited for alpha spectrometry. One-mL samples, obtained by evaporation or dissolution containing ⁶³Ni, ⁵⁵Fe, ⁹⁰Sr, and ¹²⁹I, were transferred to LSC vials for mixing with either OptiPhase HiSafe 2 or OptiPhase HiSafe 3 (PerkinElmer, USA) cocktail. An external standard quench correction was applied for activity determination. ¹²⁹I was below the detection limit; however, measurement of ¹³¹I was possible in coolant samples. Activities of difficult-to-measure radionuclides were used for calculating scaling factors for ¹³⁷Cs and ⁶⁰Co.

INTRODUCTION

The Ignalina nuclear power plant (INPP) has operated 2 RBMK-1500 reactors since 1983. This type of nuclear reactor is unique as there are only 2 such units in the world. From the point of view of radioactive waste formation, it is important to assess the quantities and composition of radionuclides generated in the RBMK-1500 reactor to resolve practical problems of radioactive waste management at present and in the future. For this task, a combined approach comprising experimental and theoretical methods was developed (Remeikis et al. 2004) in which selected waste samples were investigated by both nondestructive (gamma spectrometry) and destructive analyses. The latter was applied for determining the following radionuclides: ³H, ¹⁴C, ⁵⁵Fe, ⁶³Ni, ⁹⁰Sr, ⁹⁹Tc, ¹²⁹I, Pu, Am, and Cm isotopes.

NPP waste can be classified into 2 groups: highly active operational waste (coolant, evaporator concentrate, ion-exchange resins) and industrial waste of low or moderate activity (concrete, metal, wood, plastics, textile, rubber, swipes). Initial sources of artificial radioactivity are fission and activation reactions taking place in fuel cladding elements and other construction materials of the reactor. The coolant is an important medium where radionuclides originate. Figure 1 presents the gamma spectrum of a fresh coolant sample containing a variety of short-lived radionuclides, mainly fission products. The gamma spectrum of the powder sample from an industrial waste container is shown in Figure 2. Here, the activation products prevail.

In this work, liquid scintillation counting (LSC) is used for measuring ⁵⁵Fe, ⁶³Ni, ⁹⁰Sr, ¹²⁹I, and ²⁴¹Pu separated from several waste matrices.

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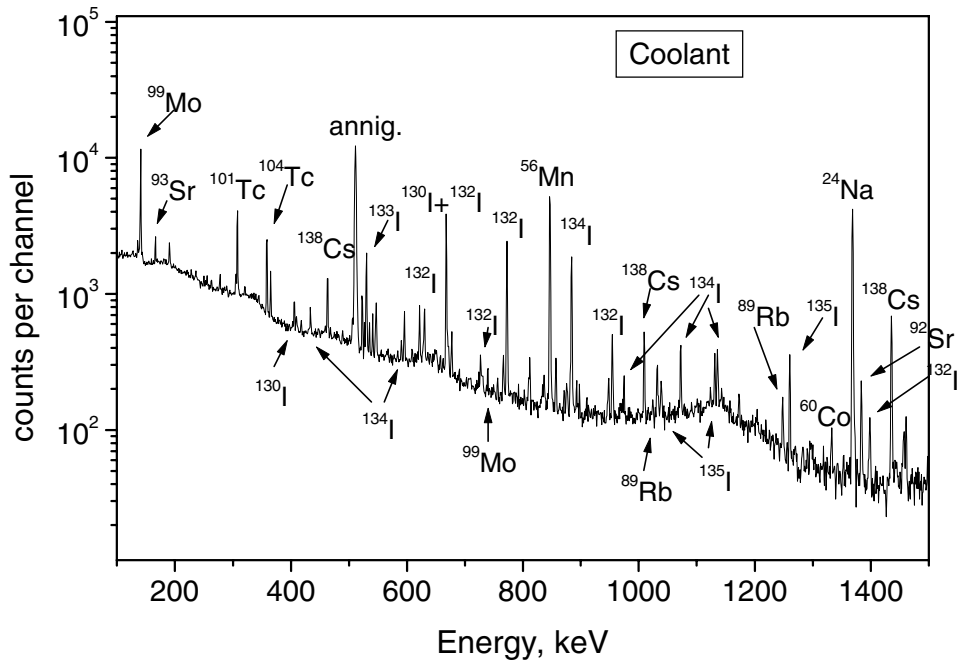


Figure 1 Gamma spectrum of the original coolant sample (elapsed time after sampling 14 min, acquisition time 300 s).

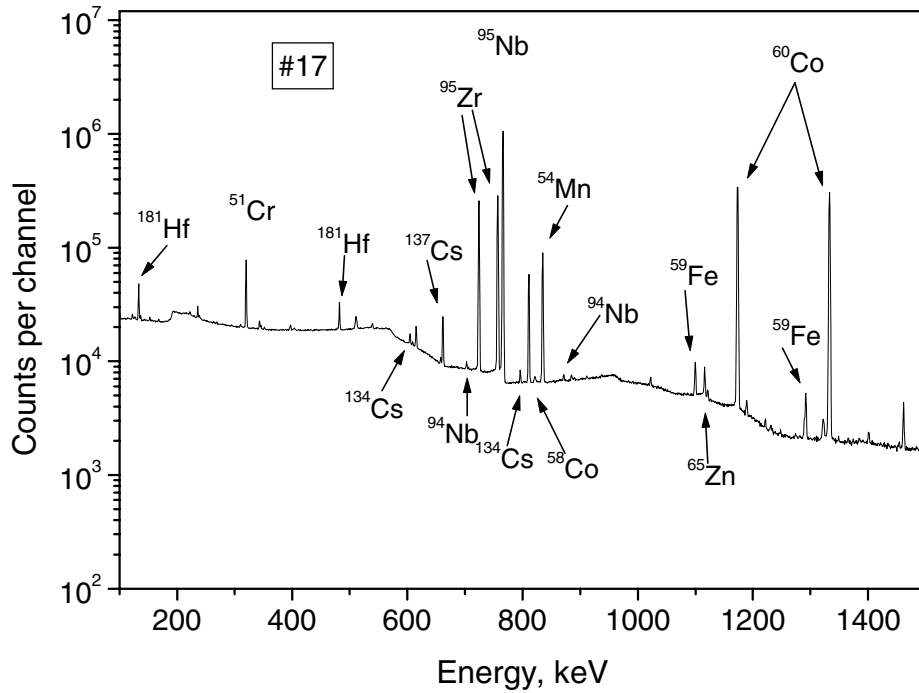


Figure 2 Gamma spectrum of the original industrial waste sample (acquisition time 50,000 s)

METHODS

Initially, samples were investigated by gamma-ray spectrometry. For coolant measurements, we used the portable MCA Inspector-2000 (Canberra Industries, Inc.) with an HPGe detector of 20% relative efficiency. Other samples were measured in laboratory conditions with the gamma spectrometer described in Gudelis et al. (2000). Decontamination factors were also determined by gamma spectrometry. For instance, the decontamination factor of Cs was better than 99.9%. Typical solid waste sample sizes ranged from 0.5 g (ion-exchange resin) to 50 g, and varied from several mL (evaporator concentrate) to 1 L (coolant) for liquid waste. After the radiochemical procedures, the samples were mixed with the LSC cocktails OptiPhase HiSafe 2 or OptiPhase HiSafe 3, and counted with the Quantulus 1220™ (Wallac). For efficiency calibration and quench curve determination, we used the reference standard solutions of ^3H , ^{55}Fe , ^{63}Ni , and ^{90}Sr , and the tritium standard was adapted for determining ^{241}Pu . The typical chemical recoveries were, respectively, 76%, 84%, 80%, 45%, and 20% for ^{90}Sr , ^{63}Ni , ^{55}Fe , ^{241}Pu , and ^{129}I . Detection limits were calculated for 1 hr of measuring time; the limits were 36, 26, 45, 70, and 150 mBq, respectively.

As an example, the quenching curves for measuring ^{55}Fe and ^{63}Ni are shown in Figure 3. Here, CCl_4 as a quenching agent was added to a mixture composed of 19 mL of OptiPhase HiSafe 3, 0.2 mL of standard solution, and 0.8 mL of distilled water. The amount of CCl_4 added ranged from 40 to 200 μL . The activity concentration of the standard for ^{55}Fe and ^{63}Ni was 98.65 Bq/g on 26 August 2003 (CERCA Framatom ANP) and 97.84 Bq/g on 1 January 2001 (NIST), respectively.

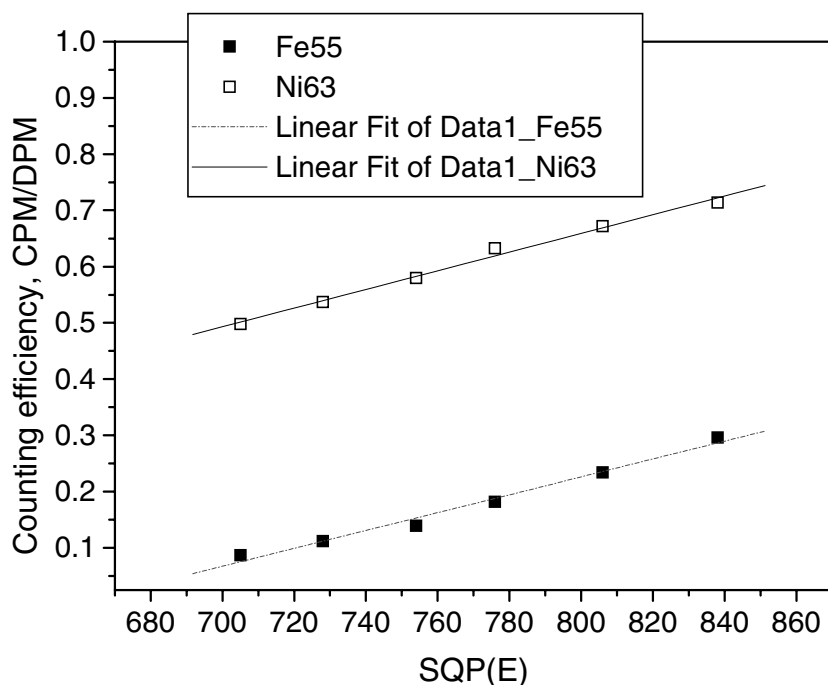


Figure 3 Quenching curve for measuring ^{55}Fe and ^{63}Ni

In our practical work with real radioactive waste samples, we employ various methods for converting the samples to a form suitable for analysis of ^{55}Fe , ^{63}Ni , and ^{90}Sr , i.e. samples are destroyed by different techniques depending upon the character of the matrix.

Some samples were placed in a high-pressure decomposition vessel with mixed acid (HNO_3+HCl) and then decomposed with a multiwave digester (PerkinElmer) for ~1 hr at 255 °C. Samples of larger mass were dried at 105 °C, then heated in a muffle furnace at 350 °C for 2 hr, and finally ashed at 550 °C for 12 hr. For some samples, wet acidic digestion was applied. Figure 4 presents the flow chart for the determination of ^{55}Fe , ^{63}Ni , and ^{90}Sr from a single sample aliquot.

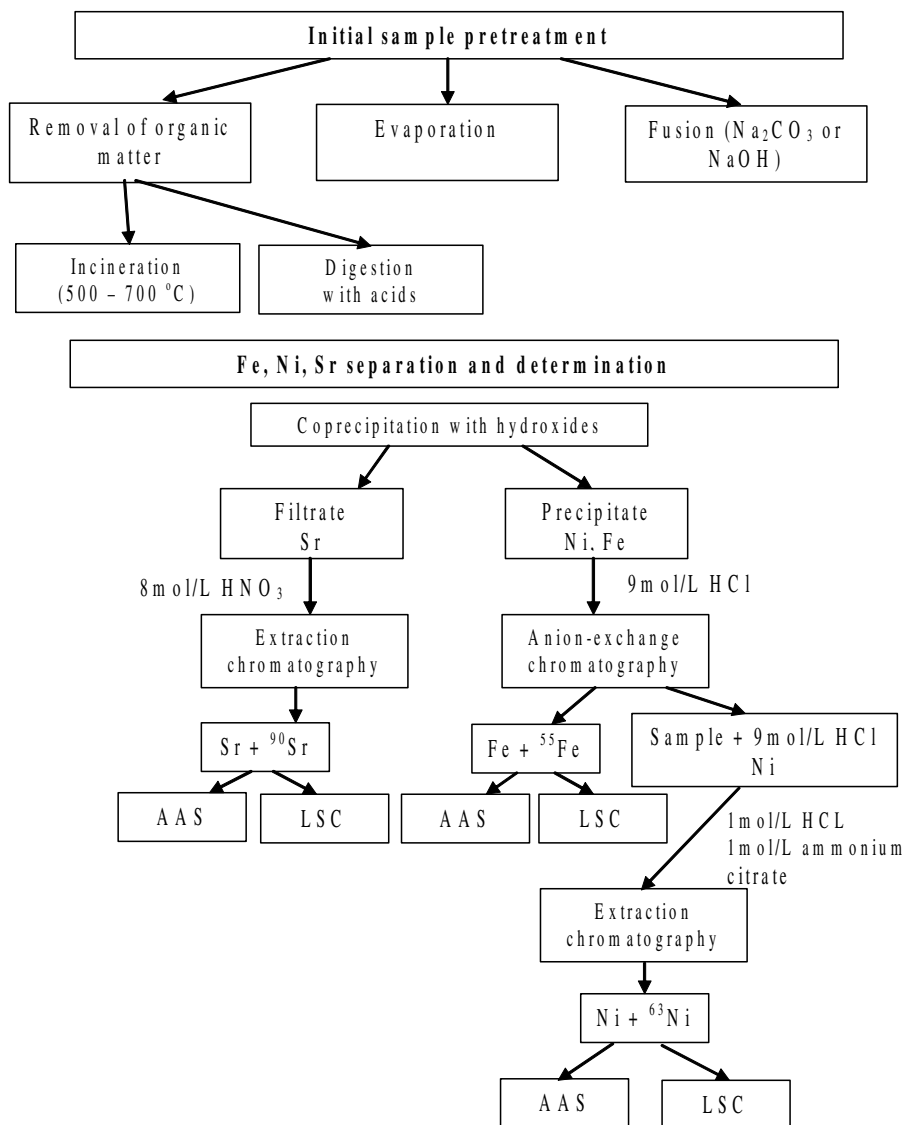


Figure 4 Flow chart of sample pretreatment and radiochemical analysis of ^{55}Fe , ^{63}Ni , and ^{90}Sr from a single sample aliquot.

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

After digestion, the amount of existing stable Fe, Ni, and Sr in a definite aliquot of the original sample was measured by an atomic absorption spectrometer (AAS) with a graphite atomizer (standard

deviation 5–10%). If stable Ni, Fe, and Sr were not present in the sample, an appropriate amount of these element-carriers was added to the sample and an analytical method was selected for separating each radionuclide or group of radionuclides.

Simultaneous determination of ^{55}Fe , ^{63}Ni , and ^{90}Sr from a single sample aliquot was successfully applied. Iron and nickel preconcentration was based on ferric hydroxide coprecipitation, which enabled Fe and Ni separation from Sr, Cs, ^3H , ^{14}C , Ba, Ca, and Cl. The supernatant (A) was left for Sr analysis.

Chemical separation of Fe from Ni, Co, Cu, Zn, and other elements was carried out by anion exchange chromatography using a strong-based anion exchange resin AG1×4, Cl^- form, 50–100 mesh. After loading the sample onto the resin preconditioned with 9M HCl in the chromatographic column (height 10 cm, diameter 1 cm), iron was rinsed via weak (0.05M) HCl or distilled water. The target for ^{55}Fe measurement was obtained by evaporating an eluate almost until dryness and by residue dissolution in 2 mol/L H_3PO_4 .

After Ni was eluted from the anion-exchange column, it was selectively separated using NiSpec columns (Vajda et al. 2003). The effective separation of ^{63}Ni from other radioelements present in the waste (such as ^{60}Co , ^{137}Cs , ^{99}Tc , and ^{90}Sr) is very important when it is necessary to accurately measure low levels of radioactivity by LSC with an associated low radioactive interference (Navarrete et al. 1995). Chugaev's classical Ni reaction with dimethylglyoxime (DMG) is very sensitive and nickel-DMG precipitate occurs on the resin in the column. The DMG complex was dissolved and eluted from the column using 10 mL of 3 mol/L nitric acid. The eluate was then evaporated until dryness, and the residue was dissolved in 2 mL of distilled water following ^{63}Ni measurement by LSC and stable Ni determination by the AAS.

Determination of ^{90}Sr

An essential step in the Sr procedure is the separation and purification of strontium, both to remove radionuclides that may interfere with subsequent β counting and to free the Sr from large quantities of inactive substances typically present. Calcium is usually the most significant of these inert constituents (Chen et al. 2002; Horwitz et al. 1991; Jeter and Grob 1994). The most common methods for strontium separation from calcium are based on differences in solubility in fuming HNO_3 (Yang et al. 2002). Furthermore, a procedure based on the insolubility of $\text{Ca}(\text{OH})_2$ in alkaline solution was also developed (Chen et al. 2002). The selective extraction of strontium can be achieved by a SrSpec (Eichrom Technologies, Inc.) chromatographic column (Horwitz et al. 1991).

In the procedure, alkaline earth elements were precipitated from the supernatant (A) by adding saturated oxalic acid and then NH_4OH to pH ~5.5. The oxalate precipitate was destroyed by treatment with 65% HNO_3 , then the solution was evaporated to dryness. The residue was dissolved in 30 mL of 3 mol/L HNO_3 and loaded on the conditioned SrSpec column. The column sizes varied from 0.6 to 1.0 cm in diameter and 6–10 cm in length, depending on the amount of dissolved solids. After some purification steps, Sr was stripped with 30 mL of distilled water and oxalate precipitate was formed by adding oxalic acid. The precipitate was dissolved with 2 mL of 1 mol/L HNO_3 . One mL of this solution was left to measure ^{90}Sr by LSC and 1 mL to measure stable Sr by AAS for recovery determination.

Determination of ^{129}I

^{129}I is very important as a sensitive tracer for large-scale environmental processes and for surveillance of reprocessing and waste conditioning plants and final waste depositories (Smidt et al. 1998).

Anthropogenic production of ^{129}I started with manmade nuclear fission processes. ^{129}I was produced in nuclear explosions, but the dominant contribution to the ^{129}I inventory results from nuclear energy production. Until 1993, European reprocessing plants emitted ~ 1070 kg (7.0 TBq) of ^{129}I over 25 yr (Yiou et al. 1994). A large amount of ^{129}I is stored in the spent reactor fuel: ~ 5660 kg (37 TBq) was estimated in 1990 (Finkel and Suter 1993).

Referring to the methods presented in previous literature (Hou et al. 1999a,b; Muramatsu et al. 1995; Verrezen and Hurtgen 1992; Schmidt et al. 1998), special preconcentration and separation methods for iodine (^{129}I) determination in the Ignalina NPP radioactive waste samples were applied:

- Usually, 1 L-volume water samples from the coolant were used for iodine determination. The sample was acidified to pH ~ 2 with HCl; 60 mg of potassium iodide was added to the sample and passed through the anion-exchange resin (AG1 \times 4, NO_3^- form). Adsorbed on the anion-exchange resin, ^{129}I was eluted with KNO_3 solution and further purified by liquid-liquid extraction using carbon tetrachloride and back-extraction with 0.02 mol/L H_2SO_3 . Purification by extraction back-extraction was carried out twice more.
- Iodine in the solid sample matrices was preconcentrated by fusion with sodium hydroxide at 700 °C. After cooling, iodine was leached with hot deionized water. KHSO_3 (0.3 mol/L) solution was used to prevent oxidation of iodide to molecular iodine. Further purification and separation were carried out by the anion-exchange chromatography and liquid-liquid extraction methods mentioned above.

The target for measurement was prepared by making an aqueous-phase alkaline (pH 9) using 0.3% LiOH and carefully evaporating to 4 mL.

Measurement of ^{241}Pu

After the α spectrometry, the disk was treated according to the procedure developed by Pimpl (1992). A stainless steel planchet was placed in a 100-mL beaker, closed with a watch-glass, and boiled for 45 min in 25 mL of 8M HNO_3 . After cooling to room temperature, the solution was transferred into a 250-mL funnel. The planchet was boiled once more in 15 mL of 3M HNO_3 , and the leach was added to the solution in the separator funnel. Plutonium was extracted by shaking the aqueous phase for 15 min with 5 mL of 0.2M TOPO/cyclohexane. After phase separation, the aqueous phase was discarded and the organic phase was washed with 25 mL of 0.5M $\text{CH}_3\text{COONH}_4$. For LSC measurement, 1 mL of the organic phase was transferred into a 20-mL polyethylene vial and 19 mL of the scintillation cocktail was added. ^{241}Pu was measured by using α/β pulse-shape analysis (PSA). Overall plutonium recovery was determined from the tracer (^{242}Pu) measurement by α spectrometry, taking into account that 99% of plutonium was redissolved from the disk. The flow chart for ^{241}Pu determination is given in Figure 5.

RESULTS AND DISCUSSION

The measured activity concentrations in the industrial waste samples varied significantly, especially in the case of activation products, where the values ranged 5 orders of magnitude. The variation of ^{55}Fe , ^{63}Ni , and ^{90}Sr activity concentration in this type of waste was 4.7–6.3E5 Bq/kg, 0.35–3.8E4 Bq/kg, and 0.1–5.8E3 Bq/kg, respectively. Higher values of activity concentration were determined in the operational waste samples. In the liquid phase of evaporator concentrate, the activity concentration of ^{55}Fe , ^{63}Ni , and ^{90}Sr varied from, respectively, 1.11E3–3.18E3 Bq/L, 1.83E4–3.44E4 Bq/L, and 120–128 Bq/L, while in the ion-exchange resins the activity concentration varied from 2.93E6–1.78E7 Bq/kg, 8.01E5–4.57E6 Bq/kg, and 3.08E4–1.13E5 Bq/kg, respectively.

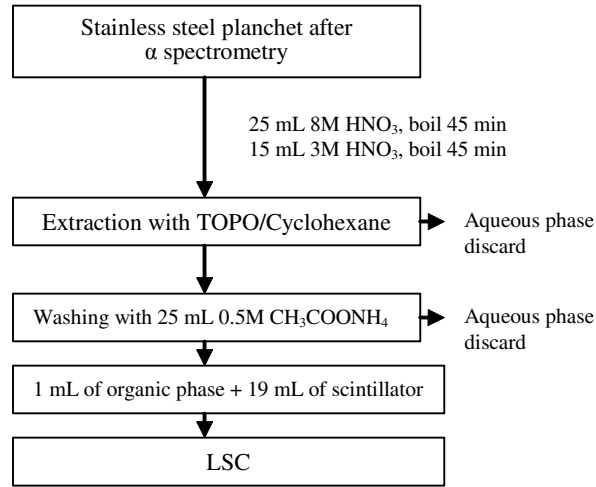


Figure 5 Flow chart of the analytical procedure for measuring ²⁴¹Pu

The typical LSC spectra of ⁵⁵Fe, ⁶³Ni, and ⁹⁰Sr separated from waste matrices are presented in Figures 6, 7, and 8, respectively. The figures confirm both the presence of investigated radionuclides in the waste and the excellent separation of elements by the methods used.

[A] 100.000 CPM/ch 29.66 min C:\DATA\DERVOS\FE-DEUVQ025200N.000 SP#12
 [B] 100.000 CPM/ch 29.65 min C:\DATA\DERVOS\FE-DEUVQ025300N.000 SP#12

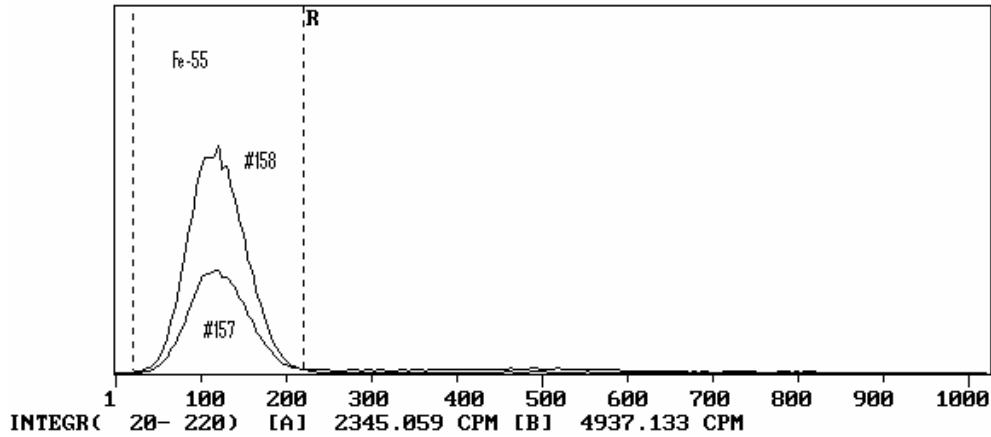


Figure 6 Examples of LSC spectra of ⁵⁵Fe separated from ion-exchange resins

[A] 20.000 CPM/ch 177.55 min C:\DATA\DERVOS\IAE-NI3Q014700N.000 SP#12
 [B] 80.000 CPM/ch 176.97 min C:\DATA\DERVOS\IAE-NI3Q014800N.000 SP#12

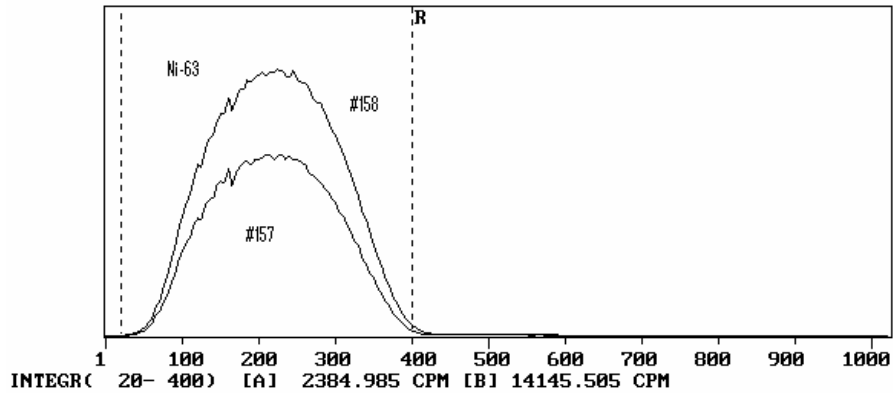


Figure 7 Examples of LSC spectra of ⁶³Ni separated from ion-exchange resins

[A] 1.500 CPM/ch 355.28 min C:\DATA\DERVOS\IAE-SR3Q014200N.000 SP#11
 [B] 3.000 CPM/ch 355.21 min C:\DATA\DERVOS\IAE-SR3Q014300N.000 SP#11

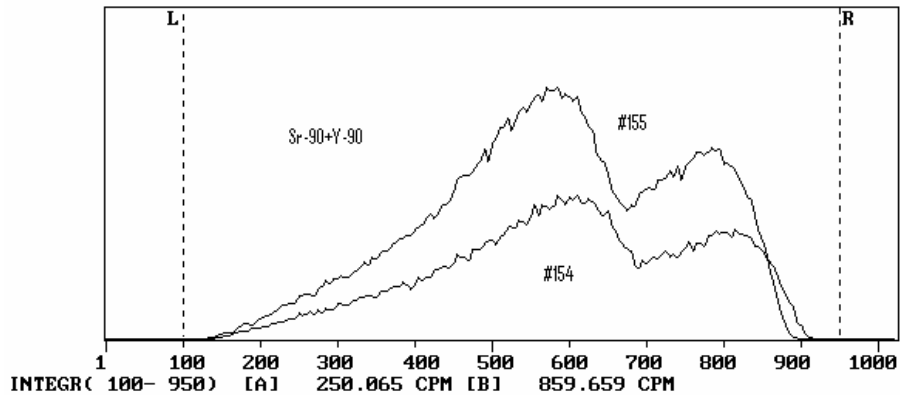


Figure 8 Examples of LSC spectra of ⁹⁰Sr separated from an evaporator concentrate (#154) and ion-exchange resins (#155).

Two LSC spectra of iodine fraction separated from the coolant are shown in Figure 9. Only ¹³¹I can be detected via LSC from 1 L of the original coolant sample. The decay follows the 8.02-d half-life value of ¹³¹I (Magill 2003). Activity of ¹²⁹I can only be inferred from the measured activity of ¹³¹I and the known fission abundances of these isotopes.

Plutonium was measured in the ion-exchange resin sample. The alpha spectrum (Figure 10) indicates the presence of ²³⁸Pu and ^{239,240}Pu, while ²⁴²Pu is used as a tracer for the chemical recovery determination. Measurement by LSC reveals the presence of ²⁴¹Pu (Figure 11), and the activity concentration of ²⁴¹Pu in this case is 5700 ± 700 Bq/kg.

[A] 12.000 CPM/ch 10.05 min C:\ARUG\I131\Q011601N.001 SP#11
 [B] 12.000 CPM/ch 29.62 min C:\ARUG\I131_3\Q011601N.001 SP#11

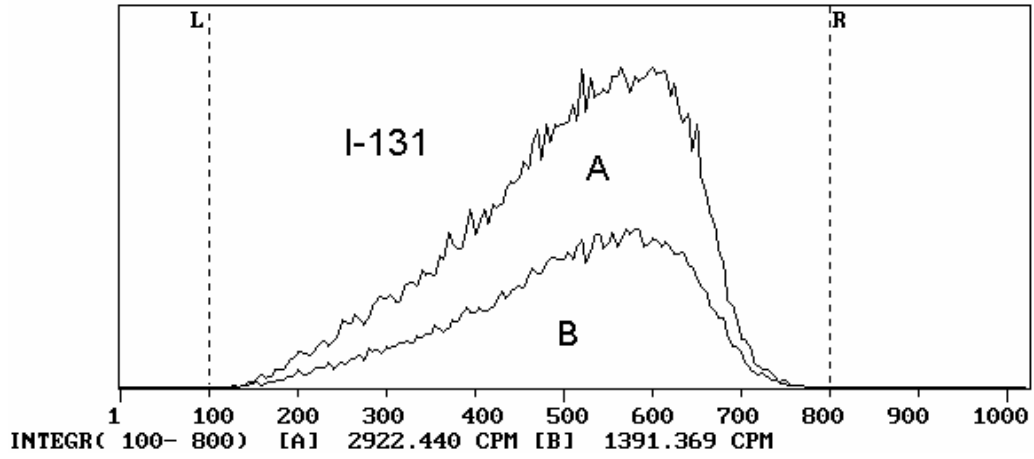


Figure 9 LSC spectra of ^{131}I separated from the same coolant sample. Spectrum A was measured on 19 April 2004, 5:06 PM; while spectrum B was measured on 28 April 2004, 9:16 AM.

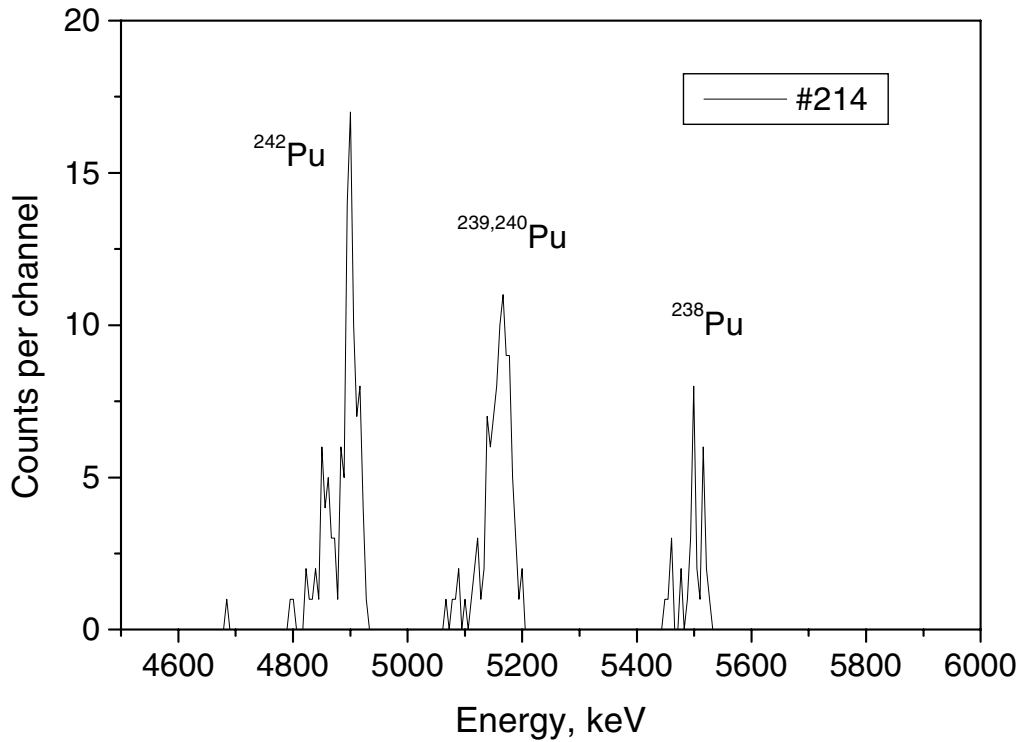


Figure 10 Alpha spectrum of plutonium separated from ion-exchange resins

[A] 0.150 CPM/ch 1183.98 min C:\ARUG\PU\#214-2\Q011000N.000 SP#11
 [B] 0.150 CPM/ch 1183.98 min C:\ARUG\PU\#214-2\Q020400N.000 SP#11

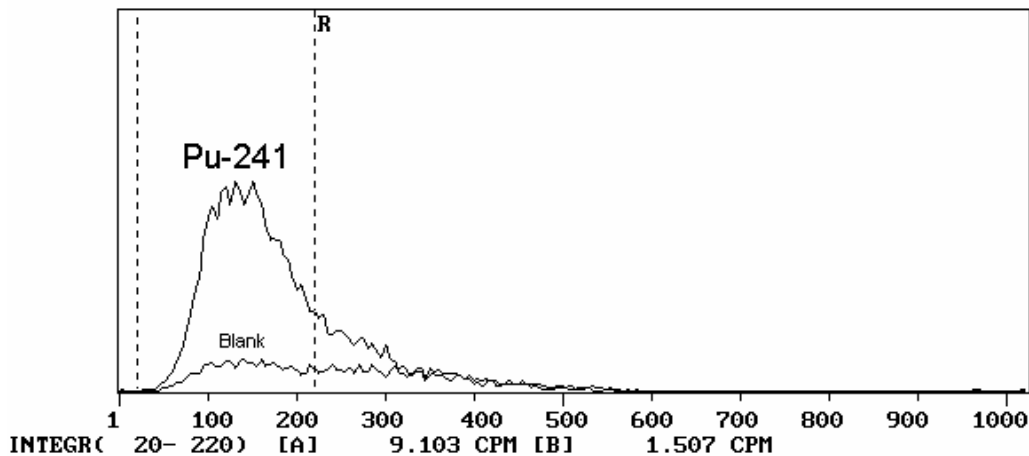


Figure 11 LSC spectrum of plutonium (sample #214) after α spectrometry (PSA = 40)

CONCLUSIONS

LSC combined with radiochemistry methods for separation of elements can be successfully applied for determining radionuclides that are difficult to quantify in nuclear power plant (NPP) wastes. Experimentally investigated ratios of difficult-to-measure radionuclides for usual gamma emitters (^{60}Co , ^{137}Cs) allow us to derive scaling factors for a particular NPP. Scaling factors are used to characterize radioactive waste and extend our knowledge about the real composition of waste.

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