

DETERMINATION OF ^{63}Ni IN LOW-LEVEL LIQUID RADIOACTIVE WASTE

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ABSTRACT. ^{63}Ni is an activation product found in radioactive wastes that is of great importance for waste treatment and long-term storage. Determination of ^{63}Ni is one part of the complex characterization of low-level liquid radioactive waste (LLRW) from the nuclear power plant (NPP) Kozloduy. Treatment and separation procedures were developed using simulated waste samples and applied to actual waste samples. Prior to separating ^{63}Ni , Cs was removed with ammonium molybdophosphate (AMP), and actinides were quantitatively separated by coprecipitation. Nickel was precipitated as a hydroxide and then purified by anion exchange and double extraction of a nickel-dimethylglyoxime complex. ^{63}Ni activity was determined by liquid scintillation counting (LSC) with the standard addition method and a counting efficiency of ~63%. For tracking down interfering elements and for yield determination of nickel, inductively coupled plasma-optical emission spectrometer (ICP-OES) measurements were performed. Interfering radionuclides were determined by gamma spectrometry. The chemical yield of ^{63}Ni determined in the actual waste samples using this procedure was ~80% and corresponded well to that of the simulated waste samples.

INTRODUCTION

A method for determining ^{63}Ni in low-level liquid radioactive waste (LL LRAW) by liquid scintillation counting (LSC) was developed and applied to alkaline liquid waste from the nuclear power plant (NPP) Kozloduy. The proposed procedure was one part of an inventory waste characterization of 15 waste storage tanks at Kozloduy that involved the determination of the 18 isotopes listed in Table 1 with their required limits of detection.

Table 1 Isotopes of interest in liquid waste.

Isotopes	Type of emission	LD (Bq/kg)
233, 234, 235, 238U	alpha	1
238, 239, 240, 242Pu	alpha	1
^{241}Am	alpha, gamma	10
242, ^{244}Cm	alpha	1
^{129}I	beta	1
^{14}C	beta	10
^{90}Sr	beta	100
^{63}Ni	beta	1000
^{55}Fe	X-ray	10
^{99}Tc	beta	10
^{94}Nb	beta, gamma	10

The radioactive liquid alkaline wastes from Kozloduy are mixtures of radionuclides, heavy metals, organic chelating agents, and detergents (potassium permanganate-consuming capacity usually was 10–20 g/L, but up to 40 g/L for some waste tanks). The only available data for the activity of the waste samples were from gamma spectrometry measurements. The average concentrations of ^{137}Cs and ^{60}Co were $\sim 3.7\text{E}+04$ and $\sim 2\text{E}+03$ Bq/mL, respectively, for most of the waste tanks.

A simulated liquid radioactive waste sample was prepared using data from gamma-spectrometry measurement protocols from the processing facility at Kozloduy and reports from the Westinghouse

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Savannah River Company (Stallings et al. 2004). Composition data of the authentic and simulated waste solutions are shown in Table 2.

Table 2 Chemical composition of the authentic and simulated waste solutions.

Component	Source	Average values for actual waste (mole/L)	Simulated waste (mole/L)
Na ⁺		3.044	2.126
	NaCl		0.31
	NaNO ₂		0.03
	NaNO ₃		1.65
	Na ₂ SO ₄		0.014
	Na ₂ CO ₃		0.51
	NaOH		pH ≈ 11
K ⁺		2.326	1.29
	KCl		—
	KNO ₃		1.29
NH ₄ ⁺	NH ₄ NO ₃	—	0.237
	NH ₄ OH		—
OH ⁻	NaOH	—	—
	NH ₄ OH		—
NO ₃ ⁻		2.666	3.177
	NaNO ₃		1.65
	NH ₄ NO ₃		0.237
	KNO ₃		1.29
NO ₂ ⁻	NaNO ₂	—	0.03
BO ₃ ⁻	H ₃ BO ₃	0.809	0.810
Cl ⁻		0.282	0.31
	NaCl		0.31
SO ₄ ²⁻	Na ₂ SO ₄	—	0.014
C ₂ O ₄ ²⁻	H ₂ C ₂ O ₄	0.10	0.1
Cit ³⁻	Citric acid	0.048	0.05
γ ⁴⁻	EDTA	0.03	0.03
Detergent	—	1 g/L	1 g/L
Sr ²⁺	SrCl ₂	—	0.0004
Cr ³⁺	Cr(NO ₃) ₃	—	0.0018
Ni ²⁺	Ni(NO ₃) ₂	—	0.0020
Cs ⁺	CsNO ₃	—	3.66E-5
Fe ³⁺	FeCl ₃	—	0.0018
Sm, Cd, Co, Sn, Sr, Cs, Y, Ce	Carrier solution for multi- nuclide gamma cocktail	—	1.3 mg/L for each metal ion

⁶³Ni is an activated corrosion product of the core and the reactor vessel construction materials and, along with ⁵⁵Fe and ⁶⁰Co, is of principal concern in radioactive waste disposal. Its long half-life (100.1 yr) makes ⁶³Ni a major source of radioactivity even 20 yr after a reactor is shut down. High levels of interfering activities, both from fission and activation products in the waste samples, pose considerable challenges to the radiochemical separation of ⁶³Ni and its accurate measurement (Lin 1996).

Sample pretreatment and matrix modification represented a critical part of the overall analysis procedure. A sequential separation procedure for ^{63}Ni was developed (Figure 1). The first step was the removal from the sample of ^{137}Cs and ^{134}Cs , the isotopes with the highest activities and dose contribution. Ammonium molybdophosphate (AMP) treatment was chosen as an initial step in reducing the gamma radiation, allowing ALARA requirements to be achieved (Koivula 2003). Ammonium molybdophosphate ($[\text{NH}_4]_3\text{PMo}_{12}\text{O}_{40}$, AMP) is an inorganic cation exchanger with a high affinity to Cs^+ ions. The selectivity of AMP for Cs is lost at pH values close to neutral, while at this pH range, divalent and tetravalent cations are picked up indiscriminately. To prevent unwanted retention of nickel, low NH_4^+ concentration is desirable. Some affinity to AMP can be expected for actinides (especially Am) if they are in ionic form. To minimize this retention, potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) was added in excess. In alkaline media, $\text{K}_2\text{S}_2\text{O}_8$ easily oxidizes actinides to their higher oxidation states (US Environmental Protection Agency 2004).

Waste samples are complex mixtures of salts and organic chelating agents at high concentrations. The complex ion formed between Ni^{2+} ion and the bidentate ligand ethylenediamine is almost 10^8 times more stable than the complex ion formed with ammonia $\text{Ni}(\text{NH}_3)_6^{2+}$ (US Environmental Protection Agency 2004). To avoid matrix interferences and to transform the presented analytes into ionic form, we applied vigorous oxidizing of the organics with an excess of $\text{K}_2\text{S}_2\text{O}_8$ and $\text{HNO}_3/\text{H}_2\text{O}_2$ mixture. The standard potential of the persulfate decomposition reaction ($\text{S}_2\text{O}_8^{2-} + 2e^- \rightarrow 2\text{SO}_4^{2-}$) is 2.01 V. Depending on the conditions, the persulfate can react with reducing agents either directly or after decomposition into SO_4^{2-} radical ions. Alkali metals and $\text{Co}/\text{H}_2\text{O}_2$ are catalysts in alkaline and acid media, respectively (Garnov et al. 2002; Egorov et al. 2004).

Two different precipitations and anion-exchange chromatography were used for further ^{63}Ni separation. In the first coprecipitation (as $\text{Ca}_2[\text{OH}]\text{PO}_4$), we quantitatively separated actinides, iron, and strontium isotopes. Nickel stayed in the supernatant as an ammonium complex. The conditions for the hydroxide precipitation and the following anion exchange ensured the separation of ^{63}Ni from Co, Cs, Mn, Cu, etc. (Lin 1996).

Finally, we purified ^{63}Ni from other interfering emitters by complexation of Ni with dimethylglyoxime (DMG), followed by double extraction in chloroform and back-extraction in dilute hydrochloric acid.

The inductively coupled plasma-optical emission spectrometer (ICP-OES) method was used to track the concentration of elements of interest and ^{63}Ni yield determination in all separation steps (US Department of Energy 1995). Activities of the interfering gamma nuclides were evaluated by gamma-spectrometry measurements.

EXPERIMENTAL

Reagents

The reagents used in the procedure were analytical grade and all are commercially available. We used the anion-exchange resin AG1×8 (100–200 mesh) from BioRad Laboratories (Richmond, USA) along with the scintillation cocktail HiSafe 3 (PerkinElmer, USA). Bidistilled water was used, and all other materials were reagent grade and were used as received. ^{63}Ni and other radioactive tracers were certified solutions.

Simulated Samples

A simulated waste solution was prepared as shown in Table 2 and aged for 4 weeks. It was then spiked with the nuclides listed in Table 3 and aged for another 4 weeks to ensure isotope exchange

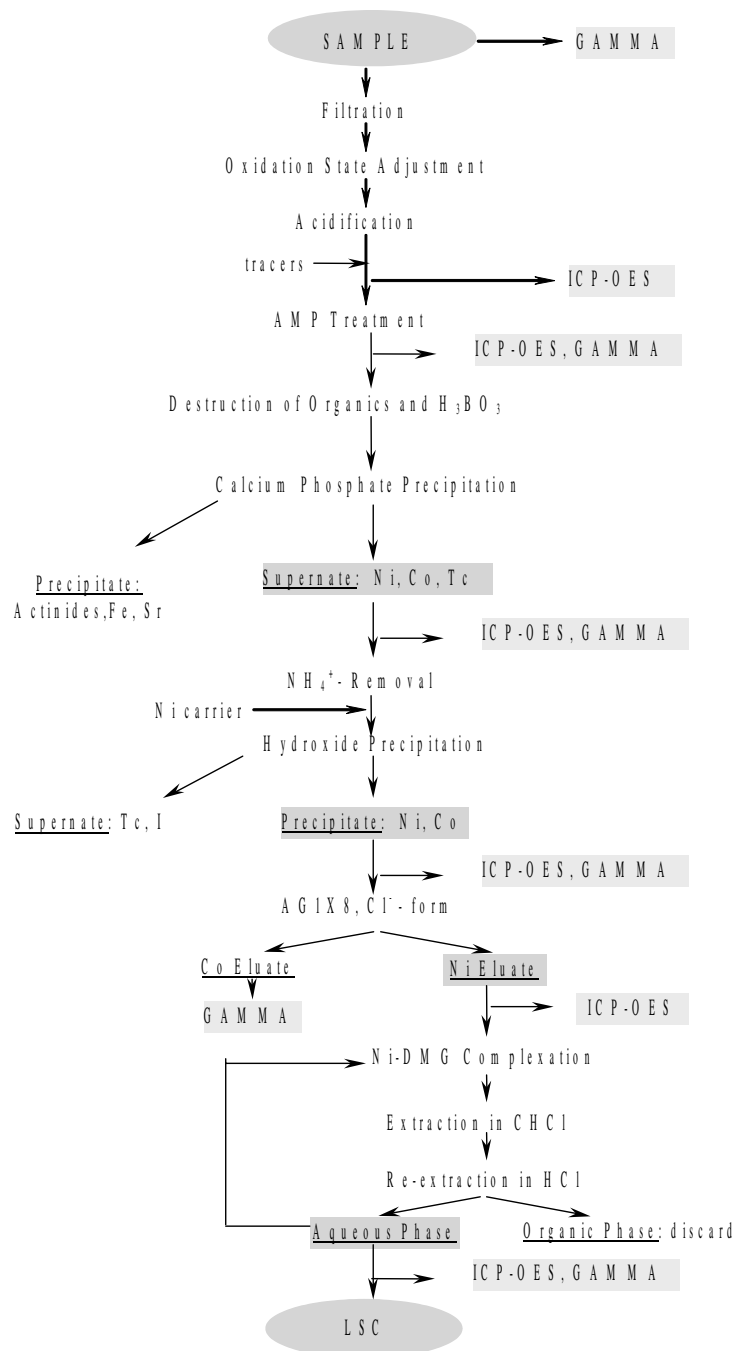


Figure 1 Separation procedure

with the carriers. ^{137}Cs and ^{60}Co (and their carriers) were added to track decontamination factors from other radionuclides at different steps of the procedure by gamma-spectrometry measurements.

Table 3 Isotope composition of the simulated waste.

Nuclide	Specific activity (Bq/g)	Nuclide	Specific activity (Bq/g)
^{238}U	8.9E-2	^{137}Cs	9.2E+0
^{232}U	6.8E-3	^{60}Co	1.8E+0
^{242}Pu	3.7E-3	^{63}Ni	7.2E+1
^{243}Am	4.0E-3	^{90}Sr	1.4E-2
^{55}Fe	1.6E+0	^{94}Nb	1.7E-1

Procedure

Simulated waste solution samples of different masses (25–100 g) were prepared and analyzed to test the final procedure for determination of ^{63}Ni in actual waste supernatant samples. Two aliquots from both simulated and actual waste solutions were taken for gamma measurements. Samples were filtered through a 0.45- μm filter, and $\text{K}_2\text{S}_2\text{O}_8$ was added in excess (0.12 g per gram of sample) to the filtrates to oxidize the actinides to their higher oxidation states. The filters were wet ashed with HNO_3 in a muffle oven at 150 °C for 30 min and at 450 °C for 1 hr, dissolved with $\text{HNO}_3/\text{H}_2\text{O}_2$, and added to the filtrates. The samples were acidified, carriers and tracers were added, and then the samples were left overnight to ensure isotope exchange. At this step, aliquots for ICP-OES measurements were taken. ^{137}Cs was removed by batching each sample with AMP slurry twice at pH = 2 for <1 min. The portions of AMP used were 800 mg (first batch) and 400 mg (second batch). We modified the AMP treatment procedure (DiPrete et al. 2003; Barnes et al. 2004) to ensure minimal retention of americium and uranium and maximum retention of Cs. ^{137}Cs retention on AMP was controlled by gamma measurement, and the unwanted removal of bi- and tetravalent ions (Ni, Sr, Fe, Mn, Cd, Tc, Ru, etc.) was controlled by an ICP-OES measurement. Before calcium phosphate coprecipitation, the samples were digested with a $\text{HNO}_3/\text{H}_2\text{O}_2$ mixture, which, along with the significant amount of potassium persulfate still present in the samples, completely destroyed the organics. Boric acid was destroyed by the multiple (5–7 times) addition of a $\text{CH}_3\text{OH}:\text{H}_2\text{O}$ (1:5) mixture. After the addition of each 12-mL portion, the samples were allowed to boil. Then, samples were diluted to 500 mL, and basic calcium phosphate precipitation was performed at a temperature near boiling with 200 mg Ca^{2+} and 120 mg PO_4^{3-} (as $(\text{NH}_4)_2\text{HPO}_4$) by the addition of a concentrated ammonia solution until pH = 9. Excess Ca^{2+} ensured complete precipitation of phosphate and coprecipitation of plutonium (Talvitie 1971). After cooling to room temperature, the precipitates were centrifuged and rinsed twice with water (the volume of rinsing water being twice the volume of precipitate) until NH_4^+ ions were completely removed. The precipitates were set aside for actinides, and ^{55}Fe and ^{90}Sr determination. The supernatants containing $\text{Ni}(\text{NH}_3)_6^{2+}$ were digested first with a $\text{HCl}/\text{H}_2\text{O}_2$ mixture and then with NaOH to remove any ammonium left in the solution and to ensure Ni^{2+} was in the ionic form. Other aliquots (10% of the sample) for gamma and ICP-OES measurement were taken. The samples were diluted, and a 3-mg Ni-carrier plus few a milliliters of c.HCl were added. The solution was then heated while stirring for about 10 min, and the pH was adjusted to 9. The samples were cooled in an ice bath and then centrifuged.

The precipitates were rinsed twice with 1M NaOH and dissolved with 15 mL of 12M HCl . To ensure better separation on the anion-exchange column, 0.5 mg of Co carrier was added. The samples were then transferred into 50-mL volumetric flasks with concentrated HCl , and 1-g aliquots for ICP-OES were taken from each sample. The ion exchange column was prepared using 10 g of AG1 \times 8 (100–200 mesh) resin in chloride form. The resin was conditioned with 6M HCl prior to separation. Then, the samples, the rinses (12M HCl), and an additional 50 mL of 12M HCl were passed through the

column to ensure complete elution of nickel. Cobalt was eluted with 10 mL of 6M HCl and 25 mL of H₂O, and these eluates were measured for ⁶⁰Co gamma activity for the real samples. Nickel fractions from the anion exchange were heated and adjusted to pH 9. To prevent coprecipitation of other metal ions with DMG, 10 mL of a 10% sodium citrate solution was added to the samples. The resulting mixture was cooled to room temperature. The samples were transferred into a 100-mL separation funnel, and a 20-mL 1% solution of dimethylglyoxime in ethyl alcohol was added. The samples were stirred, and Ni-DMG was extracted in chloroform. Nickel was then back-extracted with four 5-mL portions of 0.1M HCl until the red color of the organic phase disappeared. The aqueous phases were passed through another extraction/back-extraction cycle. After this final step, aliquots for ICP-OES yield determination, gamma spectrometry, ⁶⁰Co/¹³⁷Cs control, and LSC measurement were taken. LSC measurements were performed in 20-mL polyethylene vials with sample aliquots and a HiSafe 3 scintillation cocktail in the ratio 2/18. The counting efficiency was determined by a set of ⁶³Ni standards. For the quenched samples, the standard addition method was used. Blank samples were run through the procedure.

RESULTS AND DISCUSSION

Sequential separation procedures often save time and labor when complex samples are analyzed. The proposed procedure for ⁶³Ni determination is part of a sequential analytical procedure for multi-isotope analysis. Optimum conditions for the pretreatment, separation, and LSC of ⁶³Ni were determined using simulated samples and applied to the analysis of actual waste samples. Table 4 summarizes the ICP-OES results for nickel recovery through the entire procedure where recoveries for each step are shown as a percentage of the recovery in previous step.

Table 4 ICP-OES results for Ni recovery; the following step is a percentage of the previous one.

Step of the procedure Sample #	Simulated samples						Actual samples	
	1	2	3	4	5	6	7	8
Initial solution	100	100	100	100	100	100	100	100
After AMP treatment	89	89	79	79	79	79	92	71
After Ca-phosphate precipitation	89	89	69	80	80	80	110	100
After hydroxide precipitation	58	83	80	29	29	27	85	92
After DMG Extraction	85	— ^a	71	86	89	83	94	70
Total	39	—	31	16	16	15	81	46

^aNi-DMG extraction failure.

Retention of Ni on AMP was low, probably due to its complexation with EDTA and the ammonium present in the sample, as well as the low kinetics of exchange between NH₄⁺ ions of AMP and Ni²⁺ ions in the solution.

One of the actual samples (#7) was analyzed after 1:2 dilution, and that sample had the lowest retention of Ni on AMP. This was attributed to the significant reduction of the ionic strength of the solution. All other samples were analyzed after 1:1 dilution, and at these conditions retention of Ni on AMP was raised to 30% (sample #8). In the presence of a strong oxidizing agent (K₂S₂O₈), the probability of having a higher retention of Ni (III) on AMP than Ni(II) is minimal (Kirby 1961). A more detailed description of the conditions was reported (Nikiforova et al. 2005).

The general conditions of the calcium phosphate coprecipitation were selected to ensure complete precipitation of phosphate ions rather than calcium because of plutonium's association with phos-

phate as a complex ion (Talvitie 1971). As Ca-phosphate precipitation was performed in high-ammonia media, a relatively high and stable yield of nickel in the supernatant was achieved (Table 4). The formation of $\text{Ni}(\text{NH}_3)_6^{2+}$ accounts for the dissolution of both nickel hydroxide and phosphate at pH 9, despite the insolubility of the NiNH_4PO_4 (Kirby 1961). The presence of $\sim 0.5\text{M}$ Na_2CO_3 in the simulated samples might be responsible for the formation of slightly insoluble carbonates, which results in some nickel losses at this step. As digestion of the organics in the pretreatment steps leads to undefined concentrations of carbonate and carbonyl ions, investigation of nickel's behavior in different carbonate media should be carried out. At the moment, we do not have enough information about carbonate concentration in the actual waste samples.

In the preliminary experiments, we applied digestion of the calcium phosphate supernatant. It readily resulted in the formation of insoluble compounds, probably complex ammonium salts (polyphosphates and some of the nitrates) of different metals. The destruction was done with either a $\text{HNO}_3/\text{H}_2\text{O}_2$ mixture or NaOH . The recovery at the $\text{Ni}(\text{OH})_2$ precipitation step strongly depended on the ammonium concentration, and it significantly decreased if there were traces of ammonium ions. Because of the poor yield at this step for some of the simulated samples (#4–6), conditions were optimized to improve the yield. For the actual waste samples, the ammonium ion was completely removed before concentrating nickel as $\text{Ni}(\text{OH})_2$. This resulted in higher recoveries for this step (85 and 92%). Ammonium concentration was checked by a spot test with Nessler's reagent. Recommended pH values for $\text{Ni}(\text{OH})_2$ precipitation were contradictory (DiPrete et al. 2003; Smit and Jacobs 1959). We strictly controlled the pH value, but at pH 7–8 formation of $\text{Ni}(\text{OH})_2$ did not occur. To avoid dissolution of $\text{Ni}(\text{OH})_2$, which was precipitated at pH 9–11, the samples were cooled in an ice bath, and the precipitate was separated from the solution as soon as possible. According to the US Department of Energy's procedure (1995), minimal quantities of Fe carrier to coprecipitate nickel as hydroxide at pH 7–8 should be added. Our results showed that for this system the amount of ammonium ions left before $\text{Ni}(\text{OH})_2$ precipitation was the most important factor in reducing nickel recovery.

Nickel hydroxide is insoluble ($K_{\text{sp}} = 2 \times 10^{-16}$) and forms a very gelatinous precipitate, which can include other nuclides due to occlusion, like cesium (Kirby 1961), or elements of similar chemistry, like cobalt. Cobalt is quantitatively present in the hydroxide precipitate. Using DMG, nickel can be quantitatively separated from cobalt if cobalt is first oxidized to Co(III). On the other hand, cobalt forms a soluble complex that reduces the sensitivity of determining Ni and increases the solubility of Ni-DMG in the aqueous phase, Co(II) having greater effect than Co(III) (Kirby 1961). Stallings et al. (2004) reported that the basic approach to the Ni-DMG column works well only for matrices with low levels of interfering nuclides (DiPrete et al. 2003). For our complex matrix with high interferences, we used an anion-exchange separation of nickel prior to DMG extraction. Nickel was separated with high recovery (average $84.7 \pm 7.7\%$) and was pure enough to be counted. (Sample #2 was excluded.) Eichrom Industry's Ni-resin can be used in future work to eliminate mixed waste.

Because of the high ^{63}Ni activity in actual samples, a lower ^{63}Ni yield is acceptable to achieve a higher purity of the final nickel fraction. The main interfering nuclide, ^{60}Co , was controlled by gamma spectrometry along with ^{137}Cs activity. Table 5 summarizes the results for ^{137}Cs and ^{60}Co gamma measurements throughout the procedure where activities decreased at each step. Results for each step are shown as a percentage of activity from the previous step.

For the samples treated with AMP at 1:1 dilution (all simulated samples and actual waste sample #8), similar results of $\sim 90\%$ Cs removal were obtained. For the sample analyzed after 1:2 dilution (sample #7), the removal was even better, $\sim 97\%$. This dilution (2:1) also gave minimal retention of

Table 5 Gamma results for ^{60}Co and ^{137}Cs activity decrease (%) at different steps in comparison to previous steps.

Sample #	Simulated waste				Actual waste	
	1	2	3	4	7	8
^{60}Co						
Initial solution	100	100	100	100	100	100
After AMP treatment	98	98	99	99	106	98
After Ca-phosphate precipitation	38	38	85	84	66	98
After Hydroxide precipitation	90	—	97	—	82	—
After Ion exchange (Co-eluate)	—	—	—	—	96	86
After DMG Extraction	1	1	0	0	3	0
<i>Total</i>	<i>0.2</i>	<i>0.2</i>	<i>0.0</i>	<i>0.0</i>	<i>0.1</i>	<i>0.1</i>
^{137}Cs						
Initial solution	100	100	100	100	100	100
After AMP treatment	8	8	8	8	3	9
After Ca-phosphate precipitation	68	68	86	20	60	98
After Hydroxide precipitation	48	—	21	—	3	—
After Ion exchange	99	100	36	—	100	100
After DMG Extraction	0	0	—	0	0	0
<i>Total</i>	<i>0.0</i>	<i>0.0</i>	<i>0.0</i>	<i>0.0</i>	<i>0.0</i>	<i>0.0</i>

nickel on AMP, and it was chosen for routine analysis. Residual ^{137}Cs stayed mainly in the supernatant after the calcium phosphate precipitation. At the $\text{Ni}(\text{OH})_2$ precipitation step, cesium, still present in the samples, was occasionally found in the gelatinous precipitate. ^{137}Cs was not retained on the anion-exchange column and followed nickel, but did not form a complex with DMG and was not extracted in chloroform. ^{137}Cs was removed completely and was not present in the final ^{63}Ni sample for counting.

We expected cobalt in liquid wastes to be both in (II) and (III) oxidation states, and we did not observe any ^{60}Co retention on AMP (Table 5) despite the reported data (Smit and Jacobs 1959). Cobalt was distributed both in the precipitate and in the supernatant at Ca-phosphate precipitation. In the high-nitrate media of the samples and in the presence of oxidizing agent ($\text{K}_2\text{S}_2\text{O}_8$), the degree of destruction of complexing agents was probably responsible for these results. ^{60}Co followed nickel in hydroxide precipitation with yields higher than 80% and was almost quantitatively removed by ion exchange and DMG extraction. After the elution of nickel from the anion-exchange column, cobalt eluate was collected and measured only for the actual waste samples (96% and 86%). Results were used to estimate the ^{60}Co decontamination factor for actual waste analysis.

The LSC was performed on a Wallac Quantulus 1220TM. The efficiency was determined with a set of ^{63}Ni standards and was in the range of 60–65% (Figure 2). The figure of merit (FM) was maximum for the window 62–436 channels, and the calculations were done for that window. For 3 of the samples, we sequentially applied 2 standard additions to verify the efficiency value. For simulated sample #2 (Figure 3), the standard additions were ~1 Bq; for actual waste sample #7 (Figure 4), they were ~3.5 Bq. Most of the samples were slightly quenched with SQP values in the range of 850–872. The SQP for the standards and blanks was in the range of 844–880. Actual waste sample #7 was more quenched (SQP = 773), and standard additions of ~10 Bq were used to calculate the counting efficiency, which was 57%.

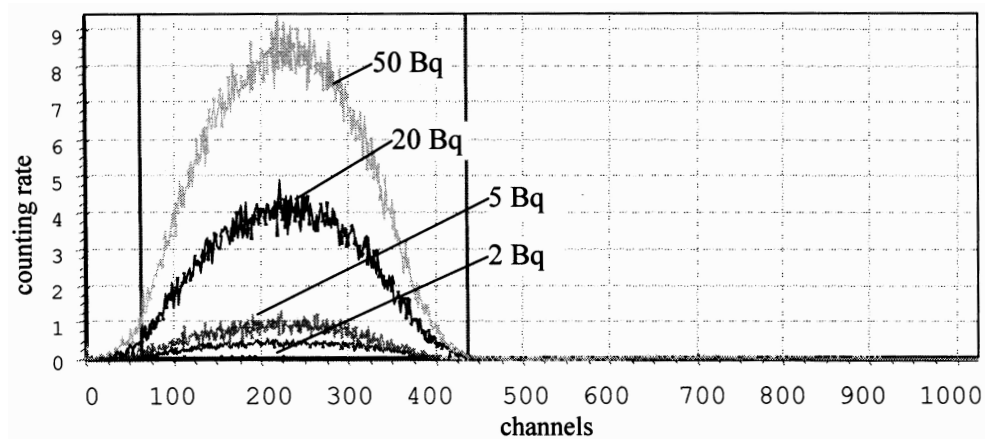


Figure 2 Spectra of standards used to calculate the efficiency

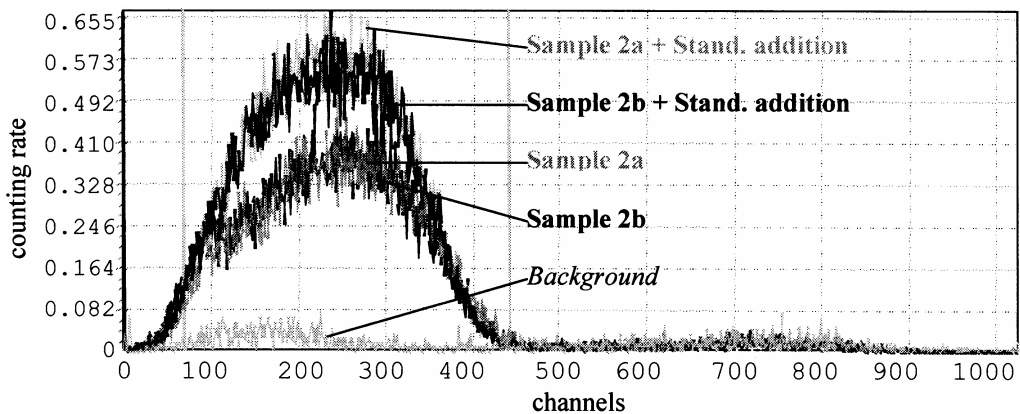


Figure 3 Two aliquots of model sample #2 with and without standard

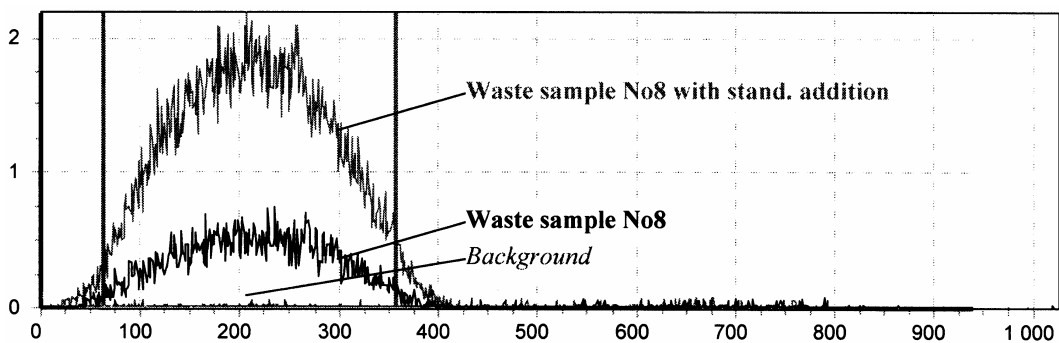


Figure 4 Spectra of real sample #8 with and without standard addition

Simulated waste samples were prepared with known nickel concentration and specific activity of ^{63}Ni . Aliquots taken at different steps of the procedure were analyzed by ICP-OES, and the mass of nickel was determined. ^{63}Ni activity concentrations were calculated using mass data and initial spe-

cific activity. A comparison of this calculation with the LSC results is shown in Table 6 and Figure 5. Uncertainties in Table 6 are combined standard uncertainties with a coverage factor $k = 1$.

Table 6 LSC data and ICP-OES calculations for the simulated samples (Bq/g).

Sample #	1	2	3	4	5	6
Initial spike	72	72	72	72	72	72
Uncertainty ($k = 1$)	2	2	2	2	2	2
ICP-OES calculation	73	73	74	74	76	76
Uncertainty ($k = 1$)	10	10	10	10	10	10
LSC	76	64	70	68	67	67
Uncertainty ($k = 1$)	5	4	5	5	5	5

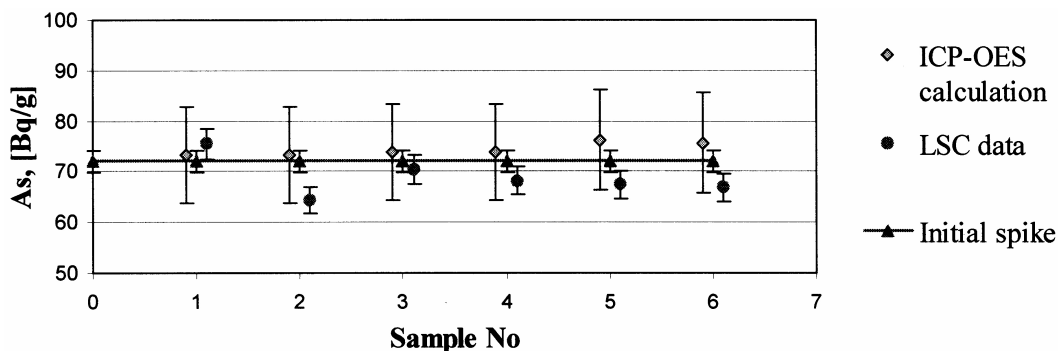


Figure 5 Comparison between LSC data and ICP-OES calculations for the simulated samples (Bq/g)

Because of the high ^{137}Cs activity of the initial solution, the first aliquots for ICP-OES were smaller than usual and also were diluted ($\text{DF} = 50$). Nickel carrier concentration was reduced considerably, and uncertainty of ICP-OES measurements for yield estimation increased (up to 15%), while the uncertainty of the LSC measurement was $\sim 5\%$. To get reproducible ICP-OES results for the first stages of the procedure, which meant more accurate yield determination for the actual samples, a nickel carrier should be added at the beginning of the analysis. The number of aliquots should be reduced to 2 at the beginning and at the end of the analysis only.

For more accurate LSC results, the presence of ^{59}Ni should be estimated. The X-ray emission ($\text{K}\alpha_1$ and α_2) of ^{59}Ni at 6.92 keV and 6.93 keV (29.8%) could appear in the LS spectrum if the ratio $^{59}\text{Ni}/^{63}\text{Ni}$ is greater than 1/40 (US Department of Energy 1995) and it would be irresolvable from that of ^{63}Ni . For this reason, a Ni-DMG planchet was prepared and counted on planer HPGe (16 mm diameter, 7 mm thick, and 2.7% counting efficiency for ^{55}Fe on the top of detector) low-energy photon spectrometer (LEPS) for one of the actual samples, but no ^{59}Ni was detected. A nickel electrodeposition procedure is under development to assay ^{59}Ni X-ray emission.

CONCLUSIONS

We developed a procedure for ^{63}Ni determination in low-level liquid radioactive wastes (LL LRAW). Using simulated samples, the procedure was tested, evaluated, and approved for analyzing actual supernatant waste from the NPP Kozloduy. Precipitation of nickel as hydroxide was opti-

mized and improved by the complete removal of ammonium ions. We chose to use ^{63}Ni determination as part of a cost-effective and time-saving sequential procedure. The results for ^{63}Ni determination in the authentic waste samples are satisfactory and will be used for characterizing LL LRAW at the NPP Kozloduy.

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