MEASUREMENT OF ALPHA/BETA RADIONUCLIDES IN SPENT ION EXCHANGE RESINS BY USING LSC METHOD

LILIANA BUJOREANU, DAN BUJOREANU, CRISTINA DIACONESCU

Institute for Nuclear Research (RATEN ICN), Piteşti, Romania
e-mail: lvasii@yahoo.com

Abstract

In this paper a method for alpha/beta radionuclides measurement in simulated spent ion exchange resins was adapted and implemented in order to be applied in real waste characterization. To measure the alpha/beta emitters by LSC (liquid scintillation counting) method, a homogenous solution has to be obtained and for this the simulated spent ion exchange resins samples were mineralized using two methods: oxidation using 307 Sample Oxidizer equipment and acid digestion in microwave field using BERGHOF SpeedWave4 equipment. Three types of solutions were used: C^{14} SPEC-CHEC solution with activity of 53690 DPM/ml, Cs^{137} solution with activity of 1220 DPM/ml and Am^{241} solution with activity of 5322 DPM/ml. During the combustion process the carbonate is flushed into the counting vial together with the liquid scintillation cocktail (PermaFluorE+) and the process gas is cached into three serial bubbler. Depending on the sample matrix, using adequate digestion reagents the solid sample is totally or partially transformed in liquid phase in the microwave digestion method. The measurements carried out on controlled labelled ion exchange resins showed an average recovery of 100.6% for C^{14}, 94.6% for Cs^{137}, and 84.7% for Am^{241}, respectively.

Keywords: *Liquid scintillation counting, Combustion, Acid digestion, Ion exchange resin*

Introduction

Generally, purification of the various circuits in a nuclear power plant (NPP) is ensured by a combination of mechanical filters and ion exchange filters. As ion exchange filters a combination of cationic, anionic and/or mixed bed resins are used depending on the circuits' physicochemical conditions and on their specific needs. After exhausting their exchange capacity, the ion-exchange resins are discharged from the purification systems. The spent ion exchange resins contain the most part of the fission radionuclides that are released by various mechanisms from the nuclear fuel as well as the activation radionuclides that are released in reactor fluids (either moderator or coolant).

A particularity of spent ion exchange resins generated by a CANDU NPP is the relatively high C^{14} content, especially in those generated in the moderator purification system. C^{14} is a long lived radionuclide (half-life of 5730 years), that is present in almost all radioactive waste streams generated by a CANDU nuclear power plant. It is a pure beta emitter that decays to N^{14} by emitting low energy beta radiation with an average energy of 49.5keV and a maximum energy of 156keV. Cs^{137} is produced by the Uranium fission and it is not a naturally occurring radionuclide. The largest source of Cs^{137} is from nuclear reactor operations. It has a half-life of 30.17 years and by disintegration to Ba^{137} it emits one to two high-energy beta particles. Am^{241} has a half-life of 432 years and emits an alpha particle with energy of 5.49 MeV. It is generated by the decay of Pu^{239} and Pu^{241} produced by neutron absorption of U^{238} [1].

Beta emitters are generally measured by liquid scintillation counting (LSC). Prior to LSC measurement, the sample to be analysed has to be converted to homogeneous and stable liquid solution and the beta emitters have to be separated.

The alpha/beta discrimination method implemented on the modern LSC counters allows for simultaneously count of alpha and beta emitting nuclides in the same sample vial.

The results can be used for the structural integrity analyses of pressure tubes in the CANDU fuel channels subject to periodic inspections in order to make a lifetime prediction.

Experimental methods

Sample preparation

For the preparation of mixed IRN150 resin, a resin that is similar to that used in the purification systems of Cernavoda NPP, the same volumetric volumes of anionic resin type IRN77 and respectively cationic resin, IRN78 were used.

To mark 4g of IRN150 resin with selected alpha/beta emitting radionuclides, the following volumes of radioactive solutions were used: 0.1 ml solution SPEC-CHEC with C^{14} activity of 53690 DPM/ml; 10 ml Cs^{137} solution with activity of 1220 DPM/ml; and 4 ml Am^{241} solution with activity of 5322 DPM/ml.

In order to label the IRN 150 resin with the radionuclides of interest, 4g of resin was contacted with 14.1 ml of radioactive solution (containing the three radionuclides) in a 50 ml syringe provided with a Millipore Millex-LCR filter. After the contacting period, needed for the radionuclide absorption on the resin, the solution was filtered through the filter and evacuated from the syringe by means of a kd Scientific model pump (see Fig.1). After filtration process, 11.5 ml of effluent was resulted and the activity measured in this effluent was used to determine the activity retained on the resin.

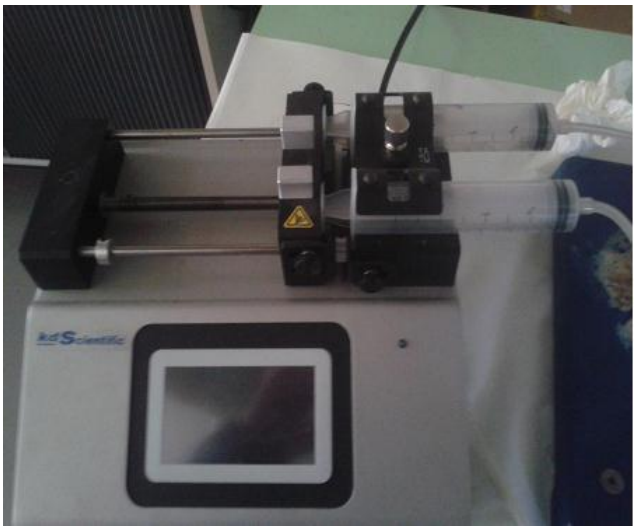


Fig.1. Contact between the resin and the mixture of radioactive solution

Since for the LSC method the sample to be analysed has to be stable, clear and homogeneous solution, obtaining of this kind of solution was the main objective of the tested sample preparation methods: sample combustion in oxygen flux and microwave acid digestion.

Experimental methods

The experimental methods applied to measure the three radionuclides in the simulated spent ion exchange resin consist of:

- ✓ Sample combustion using 307 Sample Oxidizer equipment [2] and C^{14}, Cs^{137} activity measurement by LSC using TriCarb3110TR liquid scintillation analyser [3];
- ✓ Sample digestion using *BERGHOF SpeedWave4* equipment [4] and C^{14}, Cs^{137} and Am^{241} activity measurement by LSC using TriCarb 3110TR liquid scintillation analyser.

By using 307 Sample Oxidizer, Model 307 PerkinElmer®, the sample is combusted in an oxygen-enriched atmosphere with a continuous flow of oxygen and any hydrogen present in the sample is oxidized to water while any carbon is oxidized to carbon dioxide.

If tritium is present, then the combustion product will be ^3H_2O; if C^{14} is present then the combustion product will be $^{14}CO_2$. The water is condensed in a cooled coil and then washed into a vial where it is mixed with an appropriate LSC cocktail while the CO_2 is trapped by vapour-phase reaction with an amine and the resulting product is mixed with an appropriate LSC cocktail. At the end of the combustion cycle, two separate samples - H^3 sample and a C^{14} sample - are trapped at ambient temperature, thus minimizing cross contamination. Carbo-Sorb® E is used to trap the released $^{14}CO_2$ in form of carbonate that is furthermore flushed into the C^{14} counting vial using the Perma-Fluor® E+ scintillator as a rinsing media. The ^{14}C activity is measured by LCS using a Tri-Carb®3110TR.

Other radionuclides present in the sample to be oxidized could reach the off-gases or could remain in the ashes generated at the end of the combustion process. Those that escape in the off-gasses could be trapped using gas washing bubblers.

Microwave digestion is usually accomplished by exposing the sample to adequate mineralization reagent (a strong acid or combination of acids) in a closed vessel and raising the pressure and temperature through microwave irradiation. This increase in temperature and pressure of the low pH sample medium increases both the speed of thermal decomposition of the sample and the solubility of the interest elements (in our case of the radionuclides) in solution. Once the interest elements are in solution, it is possible to quantify them by appropriate spectrometric techniques. Microwave digestion method has to be applied with caution in the case of volatile radionuclides (i.e. C^{14}, H^3, I^{129} etc.).

The speed of this heating process depends on the total volume of liquid in the oven as well as on the amount of microwave radiation applied (power). The acid mixture heating results in the creation of vapour pressure. The degree of this vapour pressure highly depends on the temperature. All digestion vessels have a maximum permissible pressure that has not to be exceed during the mineralization process

Results and discussions

Analysis of the alpha/beta activity in the effluent resulted in the preparation of the simulated spent resin

The radiochemical characterization of the effluent resulted after the radionuclide transfer from the solution to the resin was performed by LSC measurements using alpha/ beta discrimination method. Prior to the LSC measurements, sub-sample of effluent was treated by combustion in order to separate the C^{14} from Cs137 (both beta emitters).

To prepare the sample for combustion process, in order to measure C^{14}, 0.1ml of effluent was used. The experimental results obtained for C^{14} measurement by LSC after combustion of the samples are reported in Table 1.

For a better accuracy of the activity measured in the off-gases, measurements by of alpha/beta discrimination method were performed both for blank sample and the solutions sampled from the gas bubblers. The obtained results are reported in Table 2 (for the blank samples) and in Tables 3, 4 and 5, respectively (for the solution sampled from the gas washing bubblers).

Table 1. Experimental data on C^{14} measurement in effluent

Sample ID	**Effluent [ml]**	**PermaFluorE$^+$ scintillation [ml]**	**Measured activity [DPM/sample]**	**Total activity in the effluent solution (11.5 ml) [DPM]**
1	0.1	10	25	2875
2	0.1	10	24	2760

Table 2. Values obtained for sample blank by alpha/beta discrimination method

Sample ID	**Sample volume [ml]**	**AB liquid scintillation [ml]**	**Hionic Fluor [ml]**	**Measurement activity [DPM/ml]**	
				α	**β**
HCl solution	1	10	-	1	29
NaOH solution	1	-	10	0	39

Table 3. Values obtained for process gases from bubbler I

Sample ID	**Bubbler I (HCl solution)**					
	Solution [ml]	**Ultima Gold AB [ml]**	**Measurement activity [DPM/ml]**		**Activity* [DPM/ml]**	
			α	**β**	**α**	**β**
1	1	10	0	27	0	0
2	1	10	0	26	0	0

* Activity calculated taking into account the activity of the blank sample

Table 4. Values obtained for process gases from bubbler II

Sample ID	**Bubbler II (NaOH solution)**					
	Solution [ml]	**Hionic Fluor [ml]**	**Measurement activity [DPM/ml]**		**Activity* [DPM/ml]**	
			α	**β**	**α**	**β**
1	1	10	0	38	0	0
2	1	10	0	37	0	0

* Activity calculated taking into account the activity of the blank sample

Table 5. Values obtained for process gases from bubbler III

Sample ID	**Bubbler III (NaOH solution)**					
	Solution [ml]	**Hionic Fluor [ml]**	**Measurement activity [DPM/ml]**		**Activity* [DPM/ml]**	
			α	**β**	**α**	**β**
1	1	10	0	36	0	0
2	1	10	0	36	0	0

* Activity calculated taking into account the activity of the blank sample

The analysis of the values presented in the above tables show that Cs^{137} initially present in the contact solution were completely retained on the resin. While both Cs^{137} and Am^{241} was completely absorbed on the resin, for radiocarbon, data presented above show that this radionuclide was only partially retained on the resin (about 48% of the C^{14}activity in the contact solution).

Experimental results obtained by sample combustion and LSC measurements

The Model 307 PerkinElmer Sample Oxidizer provides a simple, automatic method of preparing samples for a liquid scintillation counter. The sample is combusted in a continuous flow of oxygen, forming water and carbon dioxide. During the combustion process, C^{14} is retained together with the PermaFluorE$^+$ liquid scintillation in a counting vial that is ready for LSC measurement while the combustion gases are washed through three bubblers coupled in series (Fig. 2).

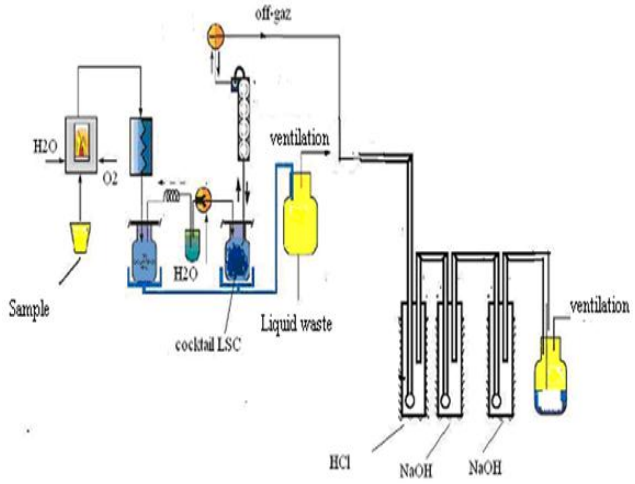


Fig.2. Flow diagram of sample preparation by combustion

The three bubblers contain the following volumes of non-radioactive solution:

- bubbler I contain 50ml of HCl 1N that is able to eventually absorb Cs^{137} that could be released in the combustion gases during the combustion;
- bubblers II and III contain 50ml of NaOH 1M that could absorb C^{14} that eventually escape during the combustion in the off-gases.

Sub-samples of 0.198g and respectively 0.2g of simulated spent resin were combusted in order to measure the C^{14} content in the special vial resulted for this radionuclide during the combustion process and the alpha/beta activity in the combustion gases.

To determine the radionuclides content in the combustion gases discharged through the off-gas system 1 ml of solution were sampled from each of the three bubblers, and the sampled solutions were mixed with 10ml of adequate liquid scintillation cocktail (see AB for acid solution and Hionic Fluor for basic solutions). The experimental results obtained for C^{14} measurement by LSC are reported in Table 6.

For a better accuracy of the activity measured in the off-gases, measurements by of alpha/beta discrimination method were performed for the solutions sampled from the gas bubblers. The blank values are the same as those reported in Table 2. The results obtained for the solution sampled from the three gas washing bubblers are reported in Tables 7 and 8, respectively.

The values presented in Tables 7 and 8 clearly show that no C^{14} was released in the process gases and the values measured in the special designed vial for this radionuclide is the one that reflect the sample C^{14} content. In the acid bubbler (bubbler I) it is expected that Cs^{137} potentially released in the process gases to be absorbed. The values measured for alpha/beta activity in the solution sampled from this bubbler are reported in the Table 9. With these values, the Cs^{137} recovery was calculated to be between 91% and 98% (see Table 10).

The sum of the C^{14} activity found in the effluent with that of the C^{14} retained on the resin is, within the limits of the experimental errors, equal to the C^{14} activity in the contact solution, indicating a high recovery for this radionuclide (Table 11).

Table 6. Experimental data on C^{14} measurement by LSC

Sample ID	**Sample weight [g]**	**PermaFluorE$^+$ [ml]**	**C^{14} Measurement activity [DPM]**	**Total sample weight [g]**	**Total C^{14} measurement activity [DPM]**
1	0.198	10	128	4	2586
2	0.2	10	130	4	2600

Table 7. Values obtained for the solution sampled from bubbler II

Sample ID	Solution weight [g]	Resin volume [ml]	Bubbler II (NaOH solution)					
			Solution [ml]	Hionic Fluor [ml]	Measurement activity [DPM/ml]		Activity* [DPM/ml]	
					α	β	α	β
1	0.198	0.155	1	10	1	39	0	0
2	0.200	0.157	1	10	1	40	0	1

* Activity calculated taking into account the activity of the blank sample

Table 8. Values obtained for the solution sampled from bubbler III

Sample ID	Solution weight [g]	Resin volume [ml]	Bubbler III (NaOH solution)					
			Solution [ml]	Hionic Fluor [ml]	Measurement activity [DPM/ml]		Activity* [DPM/ml]	
					α	β	α	β
1	0.198	0.155	1	10	1	37	0	0
2	0.200	0.157	1	10	1	37	0	0

* Activity calculated taking into account the activity of the blank sample

Table 9. Experimental data on alpha/beta measurement in solution sampled from bubbler I

Sample ID	Solution weight [g]	Bubbler I (HCl solution)					
		Solution [ml]	Ultima Gold AB [ml]	Measurement activity [DPM/ml]		Activity* [DPM/ml]	
				α	β	α	β
1	0.198	1	10	1	40	0	11
2	0.200	1	10	1	41	0	12

* Activity calculated taking into account the activity of the blank sample

Table 10. Efficiency recovery of Cs^{137}

Sample ID	Sample weight [g]	Cs^{137} Measurement activity* [DPM]	Cs^{137} Measurement Activity in 50ml HCl solution [DPM]	Total sample weight [g]	Cs^{137} Activity in total sample weight [DPM]	Cs^{137} Theoretical activity [DPM/ml]	Efficiency recovery [%]
1	0.198	11	550	4	11111.1	12200	91.07
2	0.200	12	600	4	12000.0	12200	98.30

Table 11. Efficiency recovery of C^{14}

Sample ID	Total activity in resin [DPM]	Total activity in effluent [DPM]	Total activity [DPM]	C^{14} Theoretical activity [DPM]	Efficiency recovery [%]
1	2586	2875	5461	5369	101
2	2600	2760	5360	5369	99.8

Experimental results obtained by sample acid digestion and LSC measurements

Since the combustion temperature is maximum 800 ^{0}C, lower than the melting temperature of Am^{241} (954 ^{0}C), during the sample combustion Am^{241} remains in the ash generated by this process. For this reason, to allow the measurement of this radionuclide, a second method for sample mineralization was tested.

This method consists of resin acid digestion in the microwave field [2]. Four digestion vessels were used in which the resin samples (0.2 g) were introduced, together with the digestion reagents (8 ml HNO_3 and 2 ml H_2O_2).

The maximum temperature of digestion of the samples was 230 ^{0}C. In each digestion vessel, 0.2 g of resin was mixed with 10 ml of digestion reagents. At the end of digestion process, each digestion vessels contained 10.2 ml of clear solution, indicating that complete resin digestion was achieved. From these solutions, 1 ml of solution was sampled and mixed with 10 ml of UltimaGold AB scintillation cocktail for LSC measurements.

For a better accuracy assessment of the Am^{241} activity, decontamination of pressure vessels was performed by washing with citric acid solution and measurement of the decontamination solutions by LSC. The values measured for the decontamination solution are reported in Table 12.

Table 12. Experimental data measurement in the decontamination sample

Sample ID	Solution $C_6H_8O_7$ [ml]	UltimaGold AB [ml]	Activity [DPM]
D1	1	19	80
D2	1	19	100
D3	1	19	80
D4	1	19	80

The results regarding the content of Am^{241} from the liquid samples resulted from the mineralization process of the resin samples, were obtained by LSC measurements, using alpha/beta discrimination method.

In order to calculate the total activity of Am^{241}, the activities obtained after measuring the solutions resulted by acid digestion of the resin samples, the activity in the decontamination solution and the activity in the effluent solution (total volume effluent = 11.5 ml) were taken into account.

In Table 13 the row data are reported, while Table 14 presents the values for Am^{241} activity in the resin sample and recovery efficiency for this radionuclide.

Table 13. Row experimental data on Am^{241} measurement in solution resulted by resin digestion

Sample ID	Solution volume [ml]	Solution activity [DPM/sample]	Total solution activity [DPM]	Activity in the decontamination solutions [DPM]	Total activity in solution [DPM]
1	10.2	70	714.0	80	794.0
2	10.2	74	754.8	100	854.8
3	10.2	70	714.0	80	794.0
4	10.2	73	744.6	80	824.6

Table 14. Experimental data on Am^{241} in resin samples

Sample ID	Total activity in resin [DPM]	Total activity in effluent [DPM]	Effluent activity [DPM]	Am^{241} Theoretical activity [DPM]	Efficiency recovery [%]
1	15880	1667.5	145	21244	82.6
2	17096	1667.5	145	21244	88.3
3	15880	1667.5	145	21244	82.6
4	16492	1667.5	145	21244	85.4

Conclusions

RATEN ICN Pitesti, as a partner in the IAEA Coordinated Research Project T13017 ″Management of Waste containing Long-lived Alpha Emitters: Characterization, Processing and Storage″ developed methodologies for characterization of spent resins containing Am^{241}.

To obtain the radiochemical characterization of the alpha and beta radionuclides, in present work experiments were performed on IRN150 ionic resins (similar to the resins used at Cernavoda NPP) labelled with radioactive solutions of C^{14}, Cs^{137} and Am^{241}.

In order to carry out the proposed experimental tests for recovering of the alpha and beta emitting radionuclides from the used ionic resins, the Sample Oxidizer Model 307 equipment was used.

The results obtained from measurements by liquid scintillation spectrometry on the samples acquired by combustion method show very good results regarding to the efficiency recovery.

The results presented in the paper show a quite high efficiency recovery for C^{14} (with an average of 100.6%).

Also, the experimental results obtained for Cs^{137} indicated a good recovery of this radionuclide, with an average value of 94.6%.

Regarding the Am^{241}, the recovery was a quite lower, an average value of the 84.7%, value that is considered satisfactory for the radioactive waste characterisation. As long as the recovery is calculated, this value can be used to correct the measurements carried out on the real radioactive waste samples.

References

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