C -14 ANALYSIS IN RADIOACTIVE WASTE BY COMBUSTION AND DIGESTION TECHNIQUES

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ABSTRACT

Carbon-14 is a long lived radionuclide (half life of 5730 years) present in almost all radioactive waste streams generated by a CANDU nuclear power plant. It is a pure beta emitter that decays to ^{14}N by emitting low energy beta-radiation with an average energy of 49.5keV and a maximum energy of 156keV. Before the beta radiation of ^{14}C can be measured from radioactive waste liquid scintillation counting (LSC), the samples must be transformed in a stable, clear and homogeneous solution. Two methods were tested for carbon-14 recovery and analysis in radioactive wastes from nuclear power plants. The combustion process is a simple automatic method of sample preparation, in which all carbon isotopes, including ^{14}C are oxidized to gaseous carbon dioxide that is subsequently trapped in form of carbonate in a column filled with a carbon dioxide absorbent. The microwave digestion is the method wherein the samples are transformed totally or partially in liquid phase depending on the sample matrix using adequate digestion reagents. The samples were counted with a normal and low level count mode liquid scintillation counter Tri-Carb3110TR. The tests performed on the simulated radwaste showed a ^{14}C recovery of 90% by combustion and higher than 75% by microwave digestion method.

Introduction

In general, a 600 MW CANDU reactor in normal operation conditions produces the following C^{14} and tritium containing radwaste types:
• spent ion exchange resins;
• spent filters;
• solid waste in the form of paper, protective clothing, rags;
• gaseous radioactive waste discharged by general ventilation;
• reactor's condensation ventilation chambers;
• molecular sieves.
Table 1 shows the concentrations of C-14 in different types of reactors and standardized on GWe and per operating year.

Table 1. *C-14 production in different types of nuclear reactors*

Reactor type	C-14 production speed (TBq/GWe · year)				
	Heat transport system	Moderator	Fuel	Reactor's structural materials	Total
CANDU	Less than 1%	20	1,1	1,9	23
PWR	Less than 1%	0,4	0,6	1,4	2,4
BWR	Less than 1%	0,4	0,6	2,3	3,3
GRAFIT	0,3	8,0	2,2	1,8	12,3

Quantities of C-14 produced in reactor systems will be found distributed in solid, liquid and gaseous radioactive waste, as shown in Table 2.

Table 2. *Distribution of C-14 on the types of waste by the type of reactor*

Reactor type	C-14 production speed (TBq/GWe · year)	Accumulating speed of C-14 inside gaseous radwaste (TBq/GWe · year)	Accumulating speed of C-14 inside solid radwaste (TBq/GWe · year)	Accumulating speed of C-14 inside fuel (TBq/GWe · year)
CANDU	23	13,1	8,8	1,1
PWR	2,4	0,4	1,4	0,6
BWR	3,3	0,4	2,3	0,6
GRAFIT	12,3	0,3	9,8	2,2

As shown, the production of C-14 in CANDU reactors in much higher compared to other types of reactors, as the main production reaction is the thermal neutron capture of O-17 and O-17 amount in heavy water moderator is much greater than in light water moderator of PWR and BWR reactors (O-17 in heavy water has a concentration of 0.058% compared to 0.037% from light water). Studies carried out in different types of reactors have led to the evaluation of C-14 concentration in radioactive waste. Exact distribution of C-14 in various radwaste is unknown [1]. However, it is estimated that the greater part of the C-14 production is discharged in the atmosphere, because this isotope is found in the form of CO_2 and only a small part of C-14 production remains in the fuel covering gas cleaning system.

Analysis methods of soft-beta emmiter radionuclides determination from radwaste

1. *"307 PerkinElmer Sample Oxidizer" combustion facility description for solid radwaste sample calcination*

"307 PerkinElmer Sample Oxidizer" combustion facility [1] is used in the radioachemistry laboratory for calcinating radwaste samples, to be subsequently measured using 3110TR liquid scintillation Tricarb analyzer. The sample is burned in an oxygen stream resulting CO_2 which is collected in a bottle used to measure the C-14 concentration using liquid scintillation analyzer. The following requirements regarding the preparation of samples for carrying the combustion operations and spectral analysis must be accomplished:

- the sample must be representative in terms of soft-beta emmiters radionuclides content;
- the sample weight must be correlated with the technical operating parameters of the combustion facility (calcination time, the volumes of chemicals used in the combustion processetc.);
- physical state of samples to be analyzed: in case of wet sampls or samples which requires a slow calcination it must be increased the burning level by using ignition substances.

Combustion facility consists of:
1. Combustion system;
2. The system of tritium ;
3. The system for collecting C-14;

4. The system of nitrogen and oxygen;
5. The programming facility.

Figure 1 is a schematic diagram used for combustion facility used to calcinate the radwaste samples to determine the C-14 content with liquid scintillation.

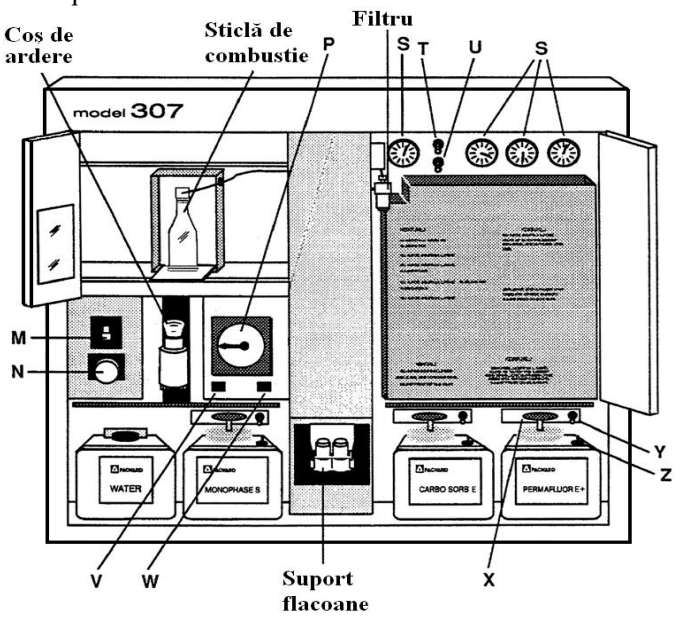

Fig. 1. *Model 307 PerkinElmer Sample Oxidizer combustion facility scheme*

where:

M – power supply switch;
N – switch on/off the facility;
P – combustion regulator: fixes the period of ignition for a complete combustion cycle;
S – pressure regulators: pressure system setting for providing oxygen, air/nitrogen and water installation;
T – toggle switch: enables tightness testing of facility circuits;
U – toggle switch: indicates the system water pressure and allows testing on leakage;
V – Switch: allows manual adjustment of combustion time, reducing the time of combustion in cases when the sample is completely ignited before the combustion reset time has expired;
X – reagent metering pumps located on the three chemicals reservoirs of the facility;
Z – reservoirs filling reactive holes;
Y – rocker switches: control the distribution of reagents to the system;
W – switch: controls the sample calcination time reset, allowing the combustion time to be prolonged in situation when the initial reset time is not enough for sample calcination.

2. TRICARB3110TR liquid scintillation analyzer description to determine the soft beta emitting radionuclides from radwaste.

Liquid scintillation measurement of radioactivity is based on the interaction of beta emitting radionuclides and the scintillator which is the component of the scintillator cocktail. Scintillator converts the ionizing radiation emitted by radionuclides into light quantum (scintillation) [2]. By placing the vials with samples analyzed in the closed detection chamber, the device measures the intensity of the photon. Emitted photons can be detected by a photomultiplier which generates a pulse signal and amplifies the voltage proportional to the number of incident photons. Liquid scintillators are organic chemicals that allow the spectral beta radiation energy to be converted in scintillation light, which can further detected by the analyzer. Due to the sample preparation, a part of the energy of disintegration can be absorbed into the

sample. Also a part of the emitted photons can be absorbed into the sample so they can no longer be detected. This phenomenon is called extinction (quench). Quench can be defined as the phenomenon of mitigation of sample photon emission, both due to chemical agents (chemical quench) [3], which reduces the efficiency of beta energy transfer from the solvent to the scintillator and due to the presence of color agents (color quench) [4], which absorb the photons emitted by the scintillator inside the sample. *Figure 2* shows a block diagram of a Tricarb 3110TR liquid scintillation analyzer.

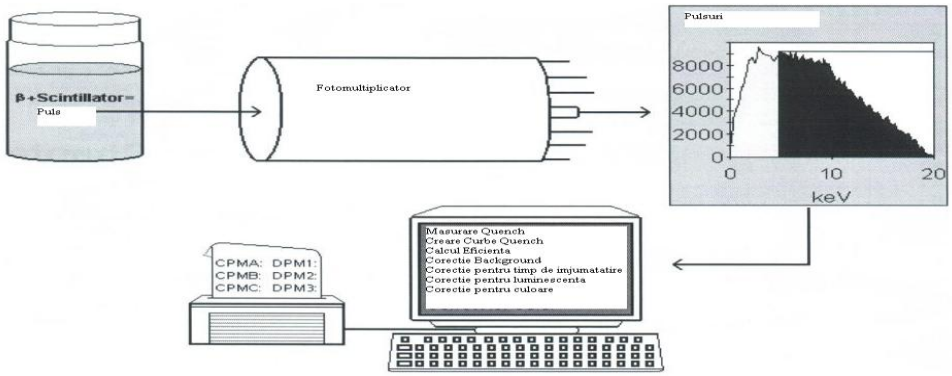

Fig. 2. *Block diagram of TriCarb 3110TR liquid scintillator analyser*

The description of BERGHOF SPEEDWAVE 4 digestion system for solid radwaste samples mineralization

Microwave field acid digestion involves decomposition of a solid material in the presence of a digestion appropriate reagent, in a microwave permeable container and resistant to high temperatures. The process involves the heating of the sample through direct absorption of microwaves by digestion reagents, solutions which normally contain ionic components. The reagents used in the digestion process can contain nitric acid, hydrochloric acid, hydrofluoric acid, phosphoric acid, sulfuric acid and other mixtures of acids, in the presence of hydrogen peroxide and water. Efficiency of digestion depends directly on the temperature at which decomposition takes place in all amount of the sample to be analyzed, on the reagent mixture and the period of time necessary to finish the digestion. Dak-model 100/4 digestion facility [5] (Figure 3) has the caps and pressure vessels made of teflon, being protected by a protective high pressure resistant ceramic layer. Magnetron frequency is 2450MHz and the microwave power can reach up to 1450W.

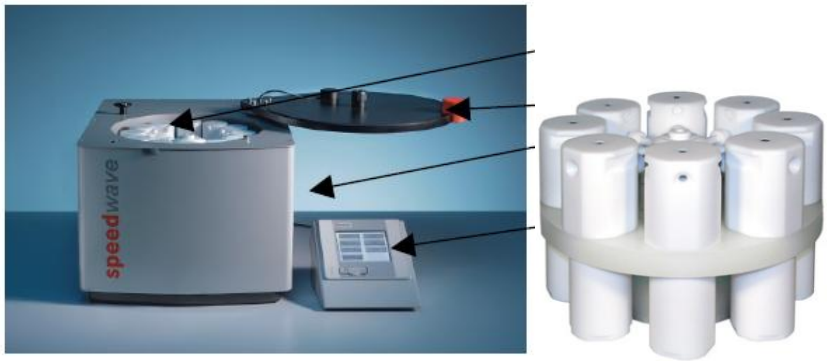

Fig. 3. *BERGHOF SpeedWave4 digestion system*

Experimental

For determining the content of C-14 in the liquid samples resulted from the mineralization process, analyzes were performed by liquid scintillation spectrometry in *Low Activity* counting mode using Tri-Carb 3110 / TR analyzer at a counting rate between 50 and 500 CPM and measurement time of minimum 1000 minutes.

Experimental results on samples of solid waste paper type

Table 4. *The results obtained on radwaste solid paper type*

Sample ID	Measuring time [min.]	Reference activity [DPM/ml]	Measured activity [DPM//ml]	Reference activity [Bq/ml]	Measured activity [Bq/ml]	Recovery efficiency [%]	*% 2s
H1(1)	1000	302.48	185	5.04	3.08	61.1	0.63
H2(1)	1000	302.48	186	5.04	3.10	61.4	0.63
H3(4)	1000	302.48	206	5.04	3.43	68.0	0.60
H4(4)	1000	302.48	206	5.04	3.43	68.0	0.60
H5(7)	1000	302.48	210	5.04	3.50	69.3	0.60
H6(7)	1000	302.48	209	5.04	3.48	69.0	0.60

where:
*%2s is the percentage of uncertainty (with confidence limits 95%) for gross counting value. As can be seen in *Table 4*, the average recovery of C-14 was approximately 66.13%. Table 5 presents the results obtained after measuring samples taken from the second bubble flusk by liquid scintillation spectrometry.

Table 5. *The results of the samples taken from the two bubble flusks*

Index probă	Activitate măsurată [DPM/proba]	Activitate măsurată [Bq/ml]
B1	18	0.03
B2	25	0.401
B(fond)	17	0.028

For an accurate assessment of C-14 experimentally determined activity besides the radiochemical analysis of the solutions from the two bubble flusks, was carried out and a decontamination of the teflon tubes by washing with a solution of citric acid, so that at the end of the process, in each tube to be samples (D), ready to be measured by the liquid scintillation spectrometry, to detect a possible contamination of digestion tube with C-14. Table 6 presents the samples preparation mode using scintillation liquids and the measurement results made by spectral analysis. Those samples were taken from the washing solution.

Table 6. *C-14 activity in samples taken from the washing solutions*

Sample ID	Decontamination solution [ml]	UltimaGold AB scintillator [ml]	Measured activity [DPM/ml]	Measured activity [Bq/ml]
D1(H)	1	19	20	0.33
D4(H)	1	19	24	0.4
D7(H)	1	19	23	0.38

As can be seen from *Tables 5* and *6*, a part of C-14 with which the samples of paper were marked on, remained on the digestion tube's walls (about 0.4 Bq / ml) and another part was released in the Off

digester gas system, explaining the low recovery efficiency of C-14 in the experiments performed with such a solid matrix type. When taking into account the C-14 activity values measured in the solutions taken from the bubble flusk vessels solutions and the one from the decontamination of digestion vessels, the recovery efficiency increases to about 81.43% (*Table 7*).

Table 7. *The recovery efficiency of C-14 after correction with the measured activity inside the bubble flusks and inside the decontamination solution of digestion vessels*

Sample ID	Reference activity [Bq/ml]	Measured activity* [Bq/ml]	Recovery efficiency %
H1(1)	5.04	3.81	75.5
H2(1)	5.04	3.83	75.9
H3(4)	5.04	4.23	83.9
H4(4)	5.04	4.23	83.9
H5(7)	5.04	4.28	84.9
H6(7)	5.04	4.26	84.5

* activity measured in solutions taken from the digestion tubes corrected with losses inside the bubble flusks and on the digestion tube's walls.

Experimental results obtained on solid radwaste textile type

Table 8. *Results of samples of solid radwaste textile type*

Sample ID	Measuring time [min.]	Reference activity [DPM/ml]	Measured activity [DPM//ml]	Reference activity [Bq/ml]	Measured activity [Bq/ml]	Recovery efficiency [%]	*% 2s
T1(1)	1000	261.82	212	4.36	3.53	80.9	0.60
T2(1)	1000	261.82	214	4.36	3.56	81.7	0.59
T3(4)	1000	261.82	195	4.36	3.25	74.4	0.62
T4(4)	1000	261.82	212	4.36	3.53	80.9	0.59
T5(7)	1000	261.82	212	4.36	3.53	80.9	0.60
T6(7)	1000	261.82	208	4.36	3.46	79.4	0.60

where:
*% 2s is the percentage of uncertainty (with confidence limits 95%) for gross counting value.

Table 9. *The recovery efficiency of C-14 after correction with the activity measured in bubble flusks and inside the digestion vessels decontamination solution*

Sample ID	Reference activity [Bq/ml]	Measured activity* [Bq/ml]	Recovery efficiency %
T1(1)	5.04	4.34	86.1
T2(1)	5.04	4.37	86.7
T3(4)	5.04	4.05	80.3
T4(4)	5.04	4.33	85.9
T5(7)	5.04	4.35	86.3
T6(7)	5.04	4.28	84.9

* activity measured in solutions taken from the digestion tubes corrected with the losses from bubble flusks and from the digestion tubes

C-14 Determination from solid radwaste using liquid scintillation spectrometry

After experiments conducted on different types of solid radwaste and presented in the previous section, the samples resulted from the combustion process were analyzed by liquid scintillation spectrometry in order to determine the C-14 content. The samples obtained are measured by spectrometry using the TriCarb3110TR liquid scintillation analyzer.

Results obtained on paper type solid radwaste

In Table 10 are shown the results obtained on paper type solid radwaste, labelled with A3, A4, A5 and in Table 11 are shown the results obtained on samples of paper type solid radwaste, labelled with A6, A7 and A8.

Table 10. *Results obtained on paper type solid radwaste*

ID.	Reference activity (DPM)	tSIE	Calculated activity (DPM)	Activity* (DPM)	Recovery efficiency (%)	Relative deviation of activity value (%)
A3	2444.5	251.29	2407	2354	96.2	3.7
A4	2444.5	176.76	2354	2302.2	94.1	3.7
A5	2444.5	130.28	2410	2356	96.3	3.5

Table 11. *Results obtained on paper type solid radwaste*

ID.	Reference activity (DPM)	tSIE	Calculated activity (DPM)	Activity* (DPM)	Recovery efficiency (%)	Relative deviation of activity value (%)
A6	2444.5	176.56	2407	2354	96.2	3.7
A7	2444.5	186.64	2436	2382.4	97.4	2.54
A8	2444.5	204.39	2424	2370.6	97	3.02

Analyzing the results shown in Table 10 and Table 11 it is noted that for all the measured samples the outcome is a high recovery rate, ranging between 94.1% and 97.4%, measurement errors being between 2.54% and 3.7%, very low values for liquid scintillation spectrometry. After the experiments and measurements carried out it was found that for a amount of fabric between 0.2-0.3g, the optimum complete combustion time is 1 minute and the optimal volumes of scintillators CarboSorb-E and PermaFluorE $^{+}$ are 8 ml respectively 12 ml per sample.

Table 12. *Results obtained on textile type solid radwaste*

ID.	Reference activity (DPM)	Calculated activity (DPM)	Activity* (DPM)	Recovery efficiency (%)	Relative deviation of activity value (%)
A9	977.8	1088	1064	99.9	8.8
A10	1955.6	2090	2044	99.9	4.5
A11	2933.4	3024	2957	99.9	0.8
A12	3911.2	3809	3724	95.2	4.7

By analyzing the results from the table 12 it is noted that for all the measured samples the outcome is a very high recovery rate (99.9%), the calculate measurement errors being between 0.8% and 8.8%, very low values for liquid scintillation spectrometry.

Experimental results obtained on oil type samples

Table 13. *Results obtained on oil type liquid radwaste*

Index probă	Timp de măsurare [min.]	Activitate referință [DPM/ml]	Activitate măsurată [DPM//ml]	Randament recuperare [%]	*% 2 s
U1(1)	1000	179.87	114	63.3	0.86
U2(1)	1000	179.87	115	63.9	0.86
U3(1)	1000	179.87	114	63.3	0.85
U4(4)	1000	179.79	144	80.0	0.76

where: *% 2s is the percentage of uncertainty (for a time confidence 95%) for gross counting value. In order to assess the efficiency of the method used in the experiments for determining the activity of radionuclide C-14, the results obtained from the analysis with liquid scintillation of samples taken from digestion solution, from the solution from bubble flusk no. 2 and from the washing solution used inside the digestion vessels, it were reported relative to the mean activity value from all three samples of radioactive oil processed inside the acid digestion facility in a microwave field. Thus, following the calculations made and shown in Table 14, the recovery efficiency of C-14 activity from radioactively contaminated oil is 82.9%.

Table 14. *The recovery efficiency of C-14 from oil samples by acid digestion*

Initial activity in oil [DPM/ml]	Measured activity in processed oil [DPM/ml]	Activity of the solution in bubble flusk no.2 [DPM/ml]	Decontamination solution activity [DPM/ml]	Total activity in the end of process [DPM/ml]	C-14 activity recovery [%]
179.88	128.88	24	0.37	153.25	85.19

Conclusion

The proposed method for the characterization of solid radwaste in terms of C-14 content by acid digestion comprises the following steps:

- ✓ mineralization of the radwaste samples in order to recover the radionuclide of interest in a solution which can be characterized by liquid scintillation spectral analysis;
- ✓ C-14 radionuclide activity measurement using TriCarb3110TR liquid scintillation analyser;

The proposed method for the characterization of radioactive waste in terms of solid content C-14 by combustion comprises the following steps:

- ✓ Radwaste sample calcination and the recovery of C-14 in the form of carbon dioxide in the presence of liquid scintillator;
- ✓ Measurement of C-14 radionuclide concentrations using the Tricarb 3110TR liquid scintillation analyzer

References

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