

IMPROVEMENT OF DIFFERENT ANALYTICAL TECHNIQUES TO CHARACTERIZE RADIONUCLIDES DIFFICULT TO MEASURE AND TOXICS IN NUCLEAR WASTE

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ABSTRACT

The decommissioning and dismantling (D&D) of nuclear facilities is a global challenge to be addressed in the future, particularly in France. In 2015, around 150 nuclear power plants were stopped or were under D&D operations. By 2050, more than half of the world nuclear capacity is scheduled to be shut down for dismantling. In consequence, high volumes of radioactive wastes are and will be produced and their management and their characterization is a key issue to be studied. In France, the National Radioactive Waste Management Agency (ANDRA) defines chemical and radiological specifications that radwaste must respect. An inventory of the compositions of the various materials encountered in radwaste, in terms of radionuclides and toxics (ex: organic ligands or toxic elements), is thus essential. For all the chemical and radiochemical characterizations requested by ANDRA, the laboratory in CEA Saclay (LASE) develops radiochemical procedures and analytical techniques to provide accurate measurements with a high confidence level and low detection limits.

1 INTRODUCTION

French stakeholders in charge of decommissioning and dismantling processes always need chemical and radiochemical characterizations of radwaste with high accuracy and sensitivity, whatever the encountered matrices (ex: steels, concretes, muds, sludges, oils). Analytical developments are always needed to be able to adapt to the evolutions of ANDRA's specifications [1]. As an example, the radiochemistry improved for Fe-55 analysis will be first described. Apart from this radiochemical procedure, the LASE laboratory has also developed the determination of C-14 speciation in liquid samples and gamma spectrometry directly on solid samples. Besides these techniques useful for laboratory, digital autoradiography has been developed for in situ and nondestructive measurements. Final examples of developments will then be presented to show very recent procedures providing analyses of organic ligands in radioactive sludges and toxic elements in organic matrices.

2 ANALYTICAL TECHNIQUES TO IMPROVE THE

CHARACTERIZATION OF RADWASTE

2.1 Analysis of Fe-55

For many years, the LASE laboratory has been involved in the characterization of radionuclides difficult to measure. Among the list of activation products, Fe-55 is one of prime interest. With a radioactive period of 2.7 years, Fe-55 is a major contributor to the radioactivity of nuclear waste in the first years of storage. Since Fe-55 disintegrates by electron capture in Mn-55 with the emission of Auger electrons and X-rays, it can be analyzed by liquid scintillation counting (LSC) but it must be isolated from the matrices and the interfering radionuclides (especially Co-60 et Ni-63) through chemical separations prior to any measurement. The reference radiochemical method of LASE laboratory is based on the extraction of the Fe-cupferron complex with chloroform followed by a back-extraction with HNO₃. As the use of chloroform is restricted through REACH regulation, an alternative protocol has been recently developed to determine Fe-55. It consists in implementing extraction chromatography where Fe is retained on TRU[®] resin and is then stripped with HNO₃ acid. This alternative method has been successfully applied to various types of radioactive waste (polymers, ion exchange resins, effluents,

sludges and steels): no bias was observed in comparison to the reference procedure. Furthermore, it provides higher decontamination factors towards actinides (see Figure 1), which is of prime interest for radwaste containing high amounts of alpha emitters.

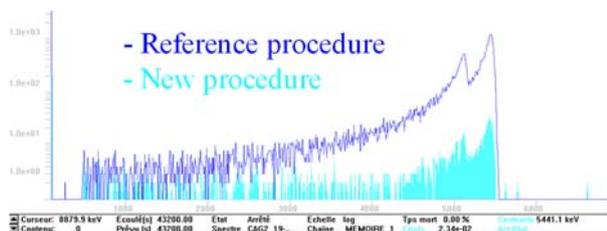


Figure 1: Alpha-spectra obtained on purified fractions with both LASE procedures dedicated to Fe-55 analysis.

2.2 Speciation of C-14: organic/inorganic partition

With a half-life of 5,730 years, Carbon-14 is a key radionuclide in safety assessments for geological disposal of long-lived waste. Based on the reaction used to make organic/inorganic partition in commercial apparatus, a method has been developed. A small volume of the aqueous sample was treated with a solution of H_3PO_4 under N_2 bubbling. The CO_2 produced from inorganic carbon was guided in a trap solution whereas organic carbon was retained in the reaction vessel.

An aliquot of the trap solution was measured by LSC to determine the amount of inorganic C-14. The remaining solution in the reaction vessel was pyrolysed to measure the concentration of organic C-14.

This procedure was tested on individual solutions and on a mixture of two C-14 labelled organic and inorganic molecules. The organic and inorganic C-14 partition results for the tests with the labelled molecules are presented in Table 1.

Table 1 Organic and inorganic C-14 partition results of labelled molecules

Sample	Trap solution (inorganic C-14)	Reaction vessel (Organic C-14)
C-14 inorganic molecule	85 %	0 %
C-14 organic molecule	0 %	100 %
C-14 inorganic molecule + C-14 organic molecule	70 %	100 %

85 % of the inorganic C-14 were trapped from the solution containing only C-14 in carbonate form and 70 % for the mixture. 100 % of organic C-14 were detected by this method for the solution containing only C-14 in glucose form and for the mixture of the two labelled molecules. The organic C-14 is not overestimated as, when a carbonate solution is used

alone, all the C-14 is detected in the trapped solution and no inorganic C-14 is kept in the vessel reaction. These tests showed that acidification by H_3PO_4 has no effect on organic C-14, releasing inorganic-14 as CO_2 with none remaining in the vessel. This method was successfully applied to various aqueous radioactive liquid waste (effluents, leachate samples of zircaloy-based alloy hulls).

2.3 Gamma spectrometry on solids

Gamma spectrometry is generally applied on samples in liquid form because standard sources are liquid. However, most wastes arriving in the laboratory are solids or sludges requiring a digestion process. This solid-liquid transition implies the use of a small amount of sample and represents a dilution of the investigated radionuclides. Thus, this limits the representativeness and increases the detection limits. Digestion may also sometimes be incomplete and then requires additional chemical steps to remove insoluble compounds. Therefore, the gamma spectrometry on solids has been developed considering directly different materials without any digestion process. The use of a software to generate curves of efficiency without source considering the physical data of the detector and a model of the sample and its environment have been tested. After a validation study based on the French NF T90-210 standard [2] using a comparison of results between a solid concrete spiked and the same concrete after digestion, the effectiveness of gamma measurements on solids with high sensitivity and without any loss of accuracy has been proven undoubtedly. Depending on the test sample, the potential gain on the detection limits varies from 1 to 100. Many more complex cases are now being studied, such as very inhomogeneous contaminated samples or particular matrices.

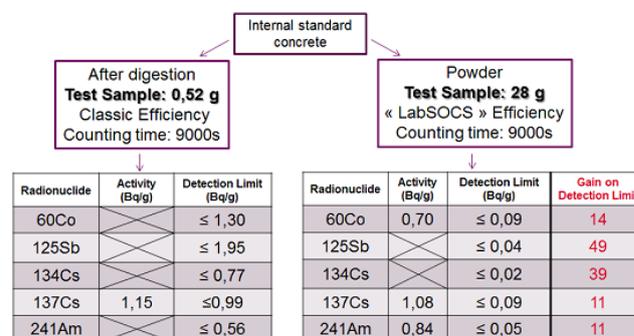


Fig 2: Comparison of results between a solid concrete spiked and the same concrete after digestion.

After initial studies on concretes, the laboratory has now extended its area of expertise to other varied matrices (graphites, metals, soils, smears ...).

2.4 In situ technique (MAUD, new device)

MAUD (Digital AUtoradiography Measurement) is dedicated to non-destructive measurement of radionuclides for decommissioning projects. The final aim of the project was to build a new industrial device (designed by ARL company France [3]) to provide image of radioactivity on surface of solid samples to be precisely controlled. MAUD is particularly focussed on measurements of alpha and beta emitters. The industrial device is composed of organic scintillators and 64 SiPM detectors to produce images of radioactivity (see Figure 3).

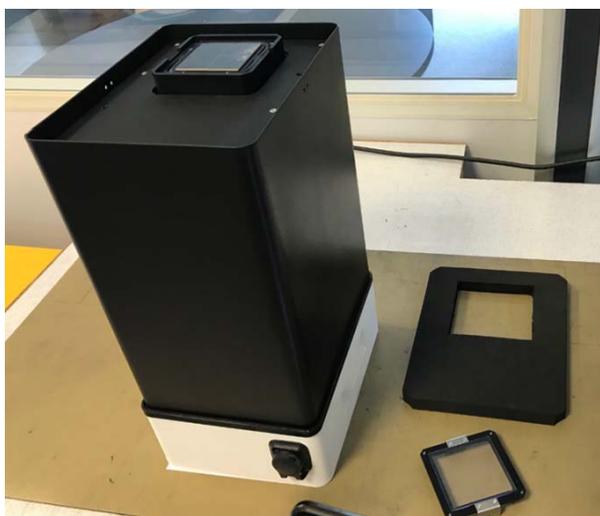


Figure 3: New MAUD device for non-destructive measurements of alpha and beta emitters for decommissioning projects.

2.5 Analysis of organic ligands

Some organic ligands such as aminopolycarboxylic acids were formerly used as decontamination agents in the nuclear industry and are now present in radioactive effluents. Due to their chelating properties, these compounds can modify the behavior of radionuclides in the environment and have to be determined in radioactive waste [1, 4]. A method based on an HPLC system coupled with ESI-MS was implemented to analyze EDTA, DTPA, NTA and TTHA in radioactive sludges containing high amounts of salts and metals. A sample treatment prior to the HPLC-ESI-MS analysis was introduced in order to eliminate radioactivity and metals. The use of internal standards enabled to correct the losses during the overall protocol (sample preparation and

analysis). As an example, Figure 4 presents the HPLC-ESI-MS chromatogram obtained for the quantification of EDTA, DTPA, NTA and TTHA in a radioactive sludge.

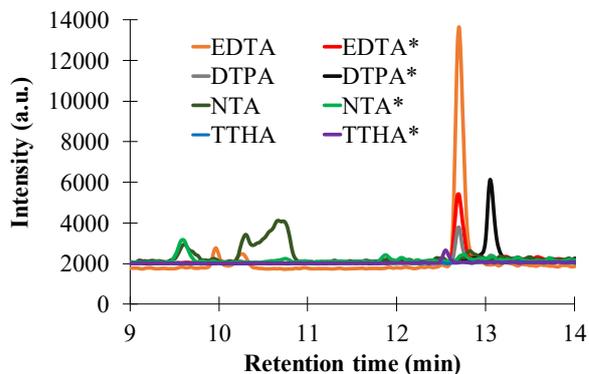


Figure 4: HPLC-ESI-MS chromatogram obtained for the quantification of aminopolycarboxylic acids (EDTA, DTPA, NTA and TTHA) in a radioactive sludge.

2.6 Analysis of toxic elements

Stakeholders in charge of waste management and particularly for complex aqueous and organic samples require analysis of toxic elements and metals, such as lead, selenium or iron. Multi elemental analysis techniques (ICP-AES and ICP-MS) are systematically used to obtain these measurements (see Figure 5). Validation methods have been implemented according to the French NF T90-210 standard [2]. For investigations of all toxic elements, quantitation limits were determined in condition of intermediate repeatability and each provided concentrations are systematically linked with an uncertainty. Round Robin Tests were also used to validate the analyses on many different matrices encountered in nuclear wastes (ex: muds, oils or waste waters).

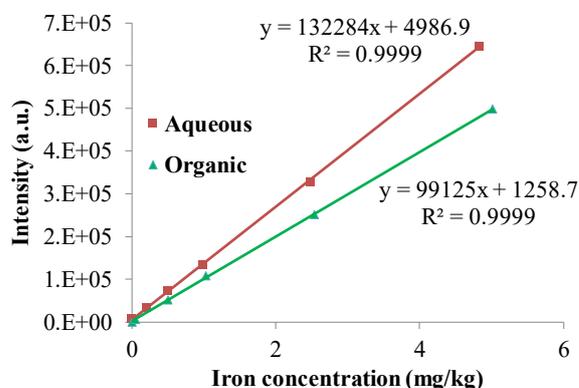


Figure 5: Calibration curves by ICP-AES obtained with aqueous and organic matrices for iron (at 259.941 nm).

3 CONCLUSIONS

The LASE laboratory improves and develops analytical techniques dedicated to the chemical and radiological characterizations of radwaste. The validation step is achieved through the participation to interlaboratory comparisons and proficiency tests and also through the contribution to the establishment of French AFNOR-BNEN standards.

ACKNOWLEDGMENTS

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