Development of different analytical techniques to investigate radionuclides difficult to measure and to improve detection limits.

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DEVELOPMENT OF DIFFERENT ANALYTICAL TECHNIQUES TO INVESTIGATE RADIONUCLIDES DIFFICULT TO MEASURE AND TO IMPROVE DETECTION LIMITS.

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Abstract: The radioactive waste management is a challenging task faced by nuclear power countries and is a prime concern for the public and therefore for control authorities. In France, several nuclear facilities were shut down few years ago and are now under dismantling. In these facilities, after the disposal of different equipments (glove boxes etc.) and a cleaning-up step, laboratories are subject to decommissioning and sometimes demolition. In order to establish the working procedure of dismantling, an inventory on the radioactive level of the various materials and areas is essential. Furthermore, correct waste classification is crucial to define the appropriate final disposal repository and also to keep disposal cost down to a minimum. For all these characterizations, the laboratory in CEA Saclay (LASE) develops radiochemical procedures and analytical techniques to provide results with high confidence level and with very low detection limits.

I. INTRODUCTION

Stakeholders in charge of decommissioning and dismantling processes always require characterizations with high confidence and sensitivity. Radiochemistry techniques are used and always developed in order to consider different matrices and different constraints. As an example, the radiochemistry developed for Ni-63 will be first described. Apart from radiochemistry allowing drastically the elimination of radionuclides hiding the signal of difficult to measure radionuclides, techniques are routinely used to provide very low level of activity. AMS technique and gamma directly on solids will be described for these applications. Besides these techniques useful for laboratory, digital autoradiography has been developed for in situ and nondestructive measurements. A final example of development will then be described to show very recent procedures providing concentration of organic ligands in radioactive sludges.

II. RADIOCHEMISTRY DEVELOPMENTS

More than fifteen radiochemical procedures are available in LASE laboratory to determine long life period radionuclides difficult to measure. The general methodology of a radiochemical protocol is depicted in Figure 1. It can be divided in three steps: 1/sample preparation and digestion, 2/matrix elimination and purification, and 3/measurements. Among the list of long-lived nuclides to be characterized, ^{63}Ni is one of prime interest. ^{63}Ni is an activation product with a radioactive period of 98.7 years. As a pure beta emitter, it must be isolated from the matrices and the interfering radionuclides (especially ^{60}Co a major radionuclide which has a similar chemical behavior) through chemical separations prior to any measurement. The reference radiochemical method of LASE laboratory is based on the extraction of the Ni-dimethylglyoxime (Ni-DMG_2) complex with chloroform followed by a back-extraction with diluted HCl. ^{63}Ni is finally analyzed by liquid scintillation counting (LSC) whereas the radiochemical yield is determined from stable Ni measured by ICP-AES. As the use of chloroform is restricted through REACH regulation, an alternative protocol has been recently developed to determine ^{63}Ni. It consists in implementing extraction chromatography where Ni precipitates on Ni® resin impregnated with DMG and is then stripped with HNO_3 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.

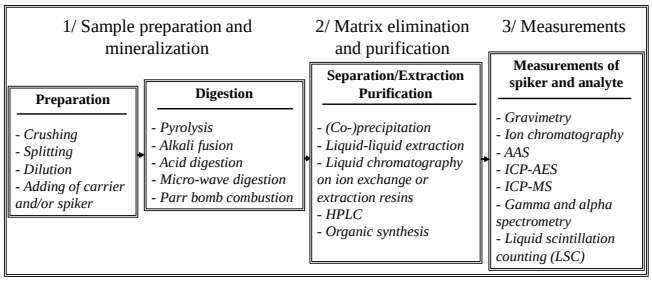


Fig 1: General methodology of a radiochemical protocol for the characterization of nuclear waste

III. ANALYTICAL TECHNIQUE TO IMPROVE SENSITIVITY

II.A. AMS

Accelerated Mass Spectrometry measurements are used to lower the detection limit particularly for Cl-36. This radionuclide is particularly important to detect with high sensitivity for the nuclear wastes repository.

As an example, the results obtained by LSC and AMS for irradiated steel samples, standard steel (8.3) and stainless stell (8.8) are gathered in Table 1.

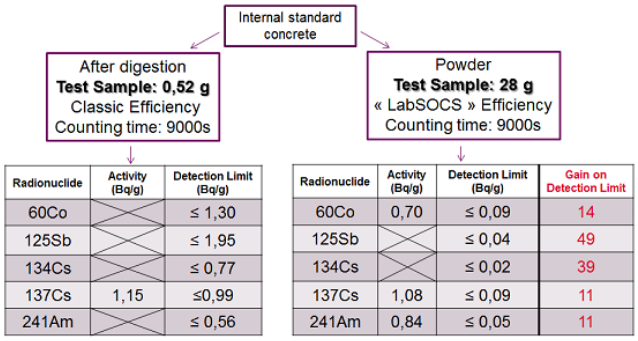
Sample	^{36}Cl (Bq/g) LSC	^{36}Cl (Bq/g) AMS
8.3	< 0.47 (DL)	2.6 10^{-3}
8.8	< 1.3 (DL)	3.7 10^{-3}

Table 1: Comparison between LSC and AMS measurement for ^{36}Cl activity on irradiated steel samples.

As we can see, AMS allows a gain of factor 170 for ^{36}Cl activity for normal steel sample and a gain of 350 for the ^{36}Cl activity on stainless steel sample.

II.B Gamma on solids

Gamma spectrometry is generally realized on samples in liquid form because standard source are liquid. However, most wastes arriving in the laboratory are solid or sludge requiring a digestion process. This solid liquid transition requires 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 recently considering directly the concrete 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 regulation NF T90-210 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 matrix.



Radionuclide	Activity (Bq/g)	Detection Limit (Bq/g)
60Co		≤ 1,30
125Sb		≤ 1,95
134Cs		≤ 0,77
137Cs	1,15	≤0,99
241Am		≤ 0,56

Radionuclide	Activity (Bq/g)	Detection Limit (Bq/g)	Gain on Detection Limit
60Co	0,70	≤ 0,09	14
125Sb		≤ 0,04	49
134Cs		≤ 0,02	39
137Cs	1,08	≤ 0,09	11
241Am	0,84	≤ 0,05	11

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

III. IN SITU TECHNIQUE

In the framework of dismantling, there is a strong need to obtain representative samples. Thus the autoradiography technique well known for biological researches has been developed. Autoradiography provides image of radioactivity by using a sensitive screen [1; 2]. Some applications were developed on potential radioactive materials such as concrete, wood, metals. The technique can investigate nuclides difficult to measure and particularly beta (H-3, C-14, Cl-36, I-129) and alphas. As an example, observation of H-3 on a piece of wood can be clearly seen in the following Figure 3.

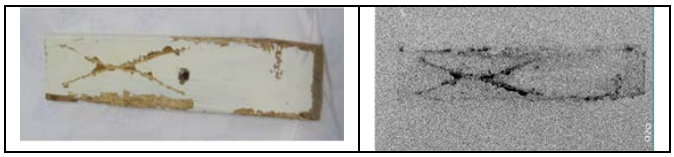


Fig 3: Image (black spots) due to tritium (present in the wood (left)) effects on autoradiography screen (right).

IV. ORGANIC LIGANDS ANALYSIS

The measurements of EDTA and gluconate [3, 4] are required for some nuclear waste. An HPLC technique coupled with ESI/MS is the analytical technique used to analyze these organic ligands. Optimized procedures including sample treatments have been developed to extract radioactivity and salts from the sludge and to convert the complexing agents in one major chelate in order to obtain an aliquot that can be injected in the HPLC-MS instrument. The sample preparation for EDTA analysis is based on the precipitation of several metals hydroxides

through a pH increase. Then, nickel is added in excess to form quantitatively Ni-EDTA which can be detected with HPLC-ESI-MS. The implementation of deuterated EDTA internal standard enabled to correct the losses during the overall protocol (sample preparation and analysis). As an example, Fig. 4 presents the HPLC-ESI-MS chromatogram obtained for the quantification of EDTA in a radioactive sludge. For gluconate, the sample treatment consists in implementing a mixed ion-exchange resin before HPLC-ESI-MS.

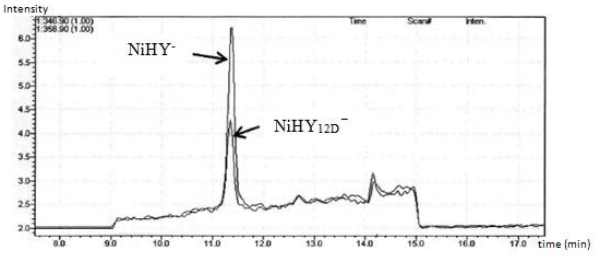


Fig 4: HPLC-ESI-MS chromatogram obtained for the quantification of EDTA in radioactive sludge ($NiHY^-$ corresponds to the negative complex of Ni-EDTA and $NiHY_{12D}^-$ corresponds to the negative complex of Ni-deuterated EDTA)

IV. CONCLUSIONS

Apart from all these developments considering radiochemistry, AMS, solid gamma, autoradiography, organic ligands, participations to round robin tests are very common to be able to compare the laboratory results with other professionals.

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NOMENCLATURE

LASE: Analytical Support to Facilities Laboratory

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