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Recent improvements in X-ray spectrometry measurements performed at the MADERE facility dedicated to reactor dosimetry requirements

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Abstract. CEA/Cadarache operates the MADERE facility dedicated to measuring the activity of radionuclides generated during the irradiation of specific dosimeters made of hyper-pure materials. This facility is equipped with seven spectrometers, two of which are dedicated to the detection of radionuclides that emit X-rays. The laboratory that operates the MADERE facility processes solid-state rhodium and niobium dosimeters, which emit X-rays of 20 keV and 16 keV respectively. In recent years, there have been significant improvements in nuclear decay data, leading to better measurement of these two X-ray emitters. A joint LDCI and LNHB thesis, defended in 2018, produced major advances (for example self-attenuation corrections for ^{93m}Nb and ^{103m}Rh). The most significant achievements and outlooks are presented in this paper for the both niobium and rhodium dosimeters.

1 Context

The Instrumentation Sensors and Dosimetry Laboratory (LDCI) that operates the MADERE facility processes solid-state rhodium and niobium dosimeters, which emit X-rays of 20 keV and 16 keV respectively. Niobium dosimeters act as reference dosimeter for the evaluation of the fast neutron fluence (E>1 MeV) (identified as an appropriate indicator for material ageing in PWRs) because of both the energy threshold of the reaction $^{93}\mathrm{Nb}(\mathrm{n},\mathrm{n}')^{93\mathrm{m}}\mathrm{Nb}$ and the long half-life of the daughter isotope (16.1 years). In addition, the $^{103}\mathrm{Rh}(\mathrm{n},\mathrm{n}')^{103\mathrm{m}}\mathrm{Rh}$ reaction on rhodium dosimeters is suitable for fast neutron fluence assessment in nuclear research reactors where activity measurements shortly after the end of irradiation are possible ($^{103\mathrm{m}}$Rh half-life of 56 minutes).

Due to the operating rules of the MADERE platform, only solid-state metal dosimeters can be measured with the spectrometry devices. The current measurement process of the niobium

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dosimeter activities [1] is a relative measurement method, which relies on the direct comparison of the activities of the sample with that of a reference dosimeter (called "working standard"). The latter is connected to a reference dosimeter (called "reference standard") provided and certified by the Laboratoire National Henri Becquerel (LNHB) - the French metrology laboratory for ionizing radiations. For this purpose, the dosimeters must have the same geometry and composition. Typically Nb dosimeters in strip form are used with a thickness of 20 µm.

In this case, the X-ray specific activity (A_i) measurement of the sample studied is given in relation to the working standard based on the following formula (1):

$$A_i = \frac{A_{work\,j}.\tau_i}{m_i.\tau_{work\,j}} \; C_{fluo\,i}\, C_{t0} \tag{1}$$

$A_{work\,j}$: Activity of the working standard *j* (Bq)
m_i: Mass of the dosimeter *i* (mg)
τ_i: Area under peak divided by acquisition time of the sampling *i* (s^{-1})
$\tau_{work\,j}$: Area under peak divided by acquisition time of the working standard *j* (s^{-1})
$C_{fluo\,i}$: Correction coefficients for fluorescence of sample i
C_{t0}: Decay correction to express the activity of the working standard on the required date

This method strongly limits the possibilities of use of these dosimeters in terms of geometry and mass: each dosimeter should have a corresponding working and reference standard to be measured. In addition, the fluorescence coefficient, depending on the irradiation and decay history of each dosimeter, has to be precisely evaluated. By 2010, the total uncertainty associated to the specific activity was significant (around 4%, k=1) and comparisons between measured activities (M) and computed activities (C) on niobium dosimeters (C/M) used in the irradiation surveillance program for French pressurized water reactors (PWRs) showed notable discrepancies in comparison with others dosimeters like iron, nickel (5 to 10%).

Unlike niobium and because of its very short half-life, rhodium dosimeters have to be measured with the classical absolute method [1] using a calibration curve and the following formula (2):

$$A_i = \frac{S_i}{m_i.\varepsilon_{det}.I_X}\, C_{sa}\, C_{fluo} \prod_i \; C_i \tag{2}$$

A_i: Activity of the working standard (Bq)
S_i: Counting rate under full-energy peak with energy "*Ei*"(s−1)
Ix: Probability of emission of the X-ray
ε_{det}: Detection efficiency at energy "*Ei*"
m_i: Mass of the dosimeter *i* (mg)
C_{fluo}: Correction coefficients for fluorescence
C_i: Correction factors (activity decay during acquisition, coincidences, and decay correction to express the activity on the required date)
C_{sa}: Self-absorption correction

The final uncertainties on the specific activity remains rather high (>5%) even though efforts have been made to perform accurate measurements of the dosimeter mass often lower than 1mg. In addition, the FLUOLE experimental programs achieved in the EOLE reactor facility [2, 3] showed up a 0.9 C/M discrepancy for the rhodium dosimeters. The uncertainty of the measured activity makes it impossible to know whether the observed C/M deviations come from the measurements or from the simulation in these FLUOLE programs.

In order to meet the accuracy requirements for the qualification of the different neutron calculation codes used for the analysis of experimental measurement campaigns in nuclear research reactors as well as the surveillance program for the French PWRs, improvements of the measurement process of the X-ray spectroscopy have been undertaken in the last ten years. The most significant achievements and outlooks are presented in this paper for both niobium and rhodium dosimeters.

2 Improvements of niobium activity measurement

Following the publication by the LNHB in 2013 of reevaluated values for the K_α and K_β emission probabilities of niobium [4] and self-attenuation coefficient per mass unit, the measurement process has since been modified accordingly in 2014. This update has resulted in a change in the measured niobium activities with a mean factor close to -7.4% in comparison with 2010 measurements. This update improved the C/M ratio for niobium from 1.10 to 1.02 in the vessel irradiation surveillance program.

The objectives of the MADERE team were then to improve the accuracy and uncertainty of niobium activity measurement by improving the evaluation of impurities induced and self-induced fluorescence yield coefficients and other correction factors (self-attenuation, geometries).

Fig. 1 gives information on the K-X-ray (16.6 keV and 18.7 keV) decay data of ^{93m}Nb.

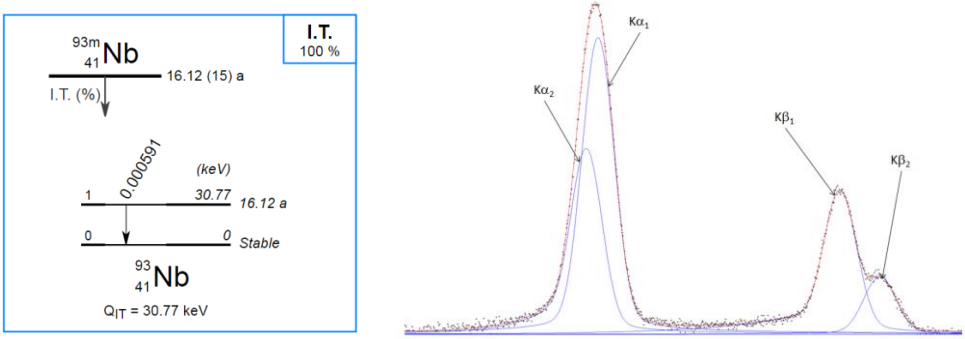

Fig. 1. Niobium Decay scheme and typical spectrum of the K-X-ray energy region of interest (impurity contributions are not displayed here)[5].

MADERE and LNHB teams have conducted the work partially through the thesis of Dr. Jonathan Riffaud [5] and continued during the post-doctoral work of Víctor Hernández-Elvira. The main results are shown in the following sections.

2.1 Evaluation of the total fluorescence yields for niobium

Both main impurities (^{182}Ta and ^{95}Mo for instance) and niobium radioisotopes (^{92}Nb, ^{94}Nb and ^{95}Nb) cause gamma emissions in the activated niobium dosimeter which induce fluorescence and contribute to an increase in the area of the full-energy peaks recorded in the spectrum of the niobium X-ray peaks. Indeed, a photon with an energy above the K-binding energy of niobium can interact by photoelectric effect in the atomic K shell. The emission of a fluorescence-induced K X-ray of niobium follows that cannot be differentiated from K X-rays characteristic of ^{93m}Nb decay. A detailed presentation of the study performed by the CEA is given in [1], [5] and [6]. Modelling calculations with GEANT 4 [11], PENELOPE [12] using PENNUC-DDEP nuclear data [14] have allowed deriving the correction factor

and its associated uncertainty (< 3%) associated to the different impurities and activation products. The validation of these calculations has been achieved through repeated activity measurements of 6 dosimeters (two different shapes and three Ta impurity levels) performed in the course of one year. Fig 2 shows the efficiency of the fluorescence correction coefficients applied to the higher impurity level.

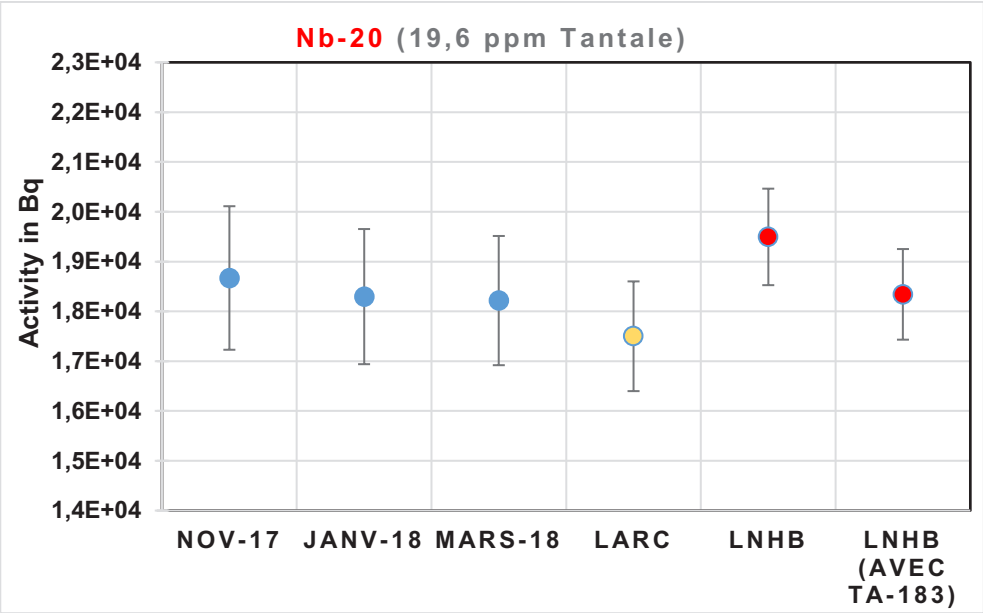

Fig. 2. Activity of ^{93m}Nb measured by MADERE platform with correction of the fluorescence of impurities and measured by LARC laboratory after dissolution measured by LNHB laboratory with and without correction of the fluorescence of impurities (Ta impurities 19.6 ppm).

These coefficients were applied in the measurements of 43 niobium samples (2 geometries and 3 Tantalum impurity concentrations) irradiated in the MARIA reactor operated by National Centre for Nuclear Research (NCBJ), Poland in the frame of second European Working Group on Reactor Dosimetry (EWGRD) round robin [7].
In conclusion, mainly ^{95m}Nb, ^{182}Ta and ^{183}Ta have a quantitative effect requiring corrections. Therefore, a low and well-characterized Tantalum content and cooling time of one before the measurement (the half-life of ^{95m}Nb being 3.61 days) are recommended.

In addition, an experimental program has been carried out at the SOLEIL synchrotron, equipped with a double Si (111) crystal in a reflection geometry, to improve the fluorescence yield (ωK) of ^{93m}Nb [5, 8]. As presented in Fig 3, the target is placed in the path of the monochromatic beam of photons with energy E_0 and intensity I_0, at an angle of incidence θ; the detector analyses the fluorescence radiation emitted at angle Φ (angles θ and Φ are defined with respect to the target surface). The incident beam is attenuated according to the linear attenuation coefficient $\mu_0 = \mu(E_0)$ and interacts with the target material at a depth x by photoelectric effect in the K layer, with probability τ_K, the effective cross section of photoelectric effect interaction. X-rays are emitted with energy E_i in all directions according to the partial fluorescence yield ω_{Ki}, where i corresponds to the α or β emission. The attenuation of the fluorescence radiation in the target material depends on the linear attenuation coefficient at the energy of the emitted radiation $\mu_i = \mu(E_i)$. These photons are measured at an emission angle Φ, in an elemental solid angle dΩ, by a silicon (SDD) or or a

high purity germanium (HPGe) detector. The total absorption efficiency ε_i of the detector having been previously determined with a relative uncertainty of about 1%, the elementary number of events, dN_i, consecutive to an interaction in an elementary thickness dx and recorded in the total absorption peak, results from :

- The absorption of the incident photon beam in the target material of elementary thickness at depth x equation (3):

$$I_0 e^{-\frac{\mu_i x}{\sin\theta}} \frac{dx}{sin\theta} \tag{3}$$

- The interaction by photoelectric effect in the K layer: τ_K
- The atomic relaxation, following this interaction, by emission of an X-ray: ω_{Ki} ;
- The absorption of fluorescence radiation emitted in the target material: $e^{-\frac{\mu_i x}{\sin\Phi}}$
- The emission of fluorescence radiation in an element of solid angle: $\frac{d\Omega}{4\pi}$
- The interaction and deposition of all the energy of the fluorescence radiation in the detector: ε_i

The total absorption efficiency can be described by the following equation (4):

$$dN_i = I_0 \tau_k \omega_{ki} e^{-\frac{\mu_0 x}{\sin\theta}} \frac{dx}{sin\theta} e^{-\frac{\mu_i x}{\sin\Phi}} \frac{d\Omega}{4\pi} \varepsilon_i \tag{4}$$

If the target is installed at 45° to the incident photon beam and the detector, and after integration over the target volume and solid angle, one can derive the partial fluorescence efficiency from N_i with equation (5):

$$\omega_{ki} = \frac{4\pi}{\Omega} \frac{N_i}{\varepsilon_i} \frac{1}{I_0 \tau_k} \quad \frac{\mu 0 + \mu i}{1 - e^{-\left(\frac{\mu_0 + \mu_i}{\sin\frac{\pi}{4}}\right)e}} \tag{5}$$

In addition, the photodiode placed beneath the target measures the current induced transmitted beam. As the efficiency of the photodiode, ε_i, was calibrated by an absolute method using a cryogenic radiometer with electrical substitution, the transmission T_i can be obtained from the target mass per unit area with equation (6).

$$T_i = e^{-\left(\frac{\frac{\mu_i}{\rho}(E_i)\frac{M}{A}}{\sin\frac{\pi}{4}}\right)} \tag{6}$$

Thus, whatever the energy E_i, the intensity I_0 of the incident photon beam is given by equation (7):

$$I_0 = C_t \varepsilon_{Pi} E_i T_i \tag{7}$$

The average total K fluorescence yield value is obtained for niobium is ω_K = 0.724 (2%). This value is in accordance with other measured values but deviates from theoretical values and by 3.6% from the value recommended by DDEP [4].

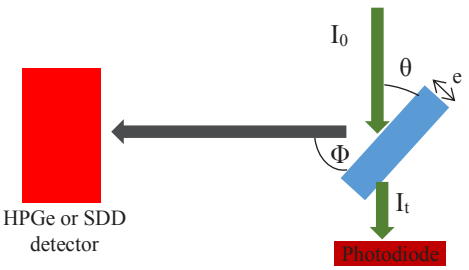

Fig. 3. Schematic of the geometry for measuring fluorescence yields.

2.2 Experimental validation of self-attenuation corrections in ^{93m}Nb

Firstly, accurate values of the mass attenuation of niobium were measured at the SOLEIL synchrotron [8]. They were measured in transmission mode using a monochromatic parallel photon beam with energy E, under normal incidence to the sample with thickness x and assuming the Beer-Lambert law. Secondly, experimental measurements of the total self-attenuation coefficient of a sample have been performed measuring the activity of a metallic sample of niobium, then dissolving this sample and re-measuring the activity of the liquid sample. Since the measurement of the liquid sample is not affected by the self-attenuation corrections, the comparison of these results provides a direct assessment of the self-attenuation coefficient to be applied to the solid sample measurements. For this purpose, three dosimeters were irradiated in the French OSIRIS reactor (operated at 70 MWth). The measurements of the solid dosimeters were performed by the MADERE platform with the relative method and by efficiency calibration curve with the three existing counting geometries (denoted as X1-E4, X2-E4 and X2-E8). The samples were then dissolved and measured by the CEA/LARC laboratory. Results shown Fig 4. illustrates the improvement in the accuracy of the activity calibration curve technique compared to the relative measurement method and to the dissolution technique.

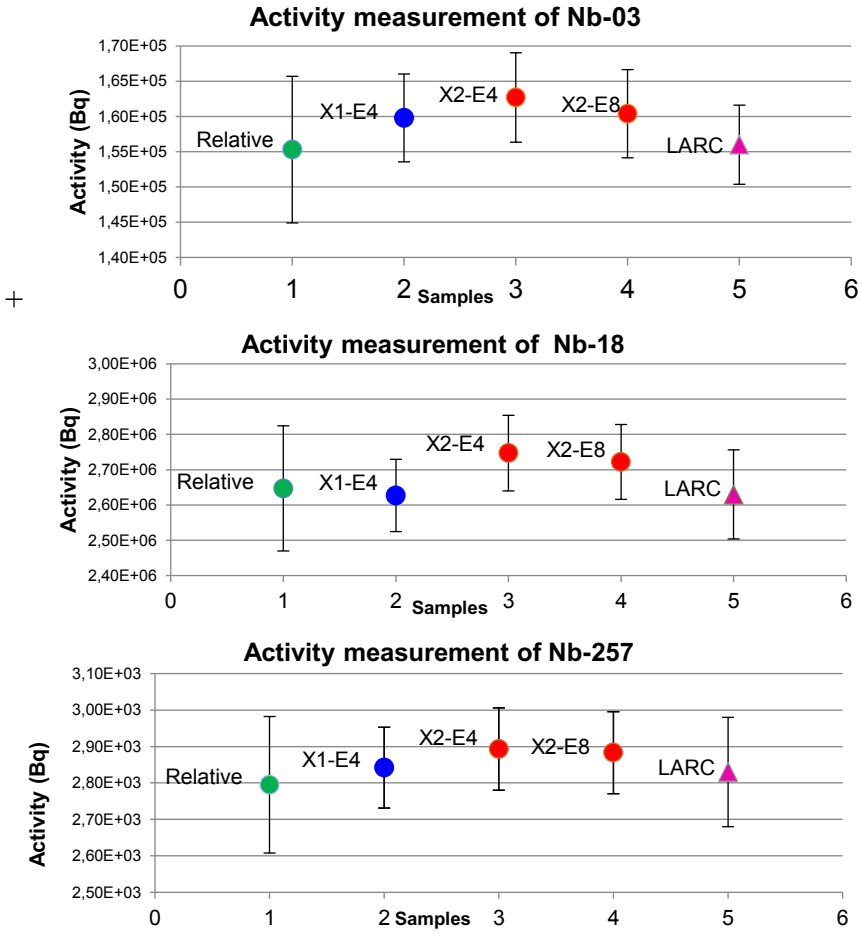

Fig. 4. ^{93m}Nb activity measurements comparison (k=1) for 3 different niobium dosimeters. LARC point corresponds to dissolution measurement.

3 Improvements of rhodium activity measurement

Following the analysis of the FLUOLE rhodium results measured with the absolute measurement method [9], a long-term R&D program has been initiated for ^{103m}Rh activity measurements aiming at updading self-attenuation and fluorescence corrections, efficiency calibration curve and nuclear data. Fig 5 gives the main features of the ^{103m}Rh decay scheme and emitted X spectrum.

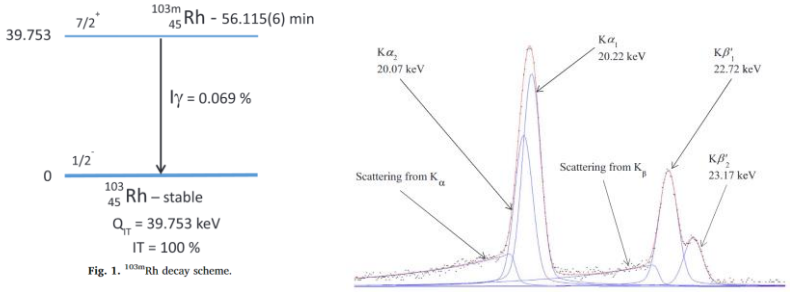

Fig. 5. ^{103m}Rh decay scheme and typical K X-ray spectrum [8].

3.1 Evaluation Self-attenuation corrections in ^{103m}Rh

Self-attenuation corrections for the K_α and K_β lines of ^{103m}Rh have been determined using empirical methods and validated first [8] by modelling calculations codes (ETNA [13], PENELOPE [12]). Experimental validation has been conducted in the SOLEIL facility, with the same measurement procedure as described above for niobium dosimeter, and analysis of the activities of two sets of three dosimeters, with respective thicknesses of 50 µm, 12 µm, and 6 µm, irradiated in two symmetrical locations under comparable neutron flux conditions in the EOLE reactor). The self-attenuation coefficients used for the K_α and K_β lines are therefore consolidated.

3.2 Evaluation of fluorescence yields and absolute K X-ray emission intensities for rhodium

Measurements performed at the SOLEIL facility, with the same methodology as the one described for the niobium dosimeters, using a rhodium target of nominal thickness 6 µm and a mass per unit area of 0.058952 g.cm^{-2}. The acquisitions were recorded over a range of incident photon energies between 24 and 30 keV with a 200 eV step, in which range the mass attenuation coefficients were previously measured as for the niobium sample. Fig. 6 shows all the results of the measurements made including the partial fluorescence yields K_α and K_β and ω_K, the average value of which is 0.786.

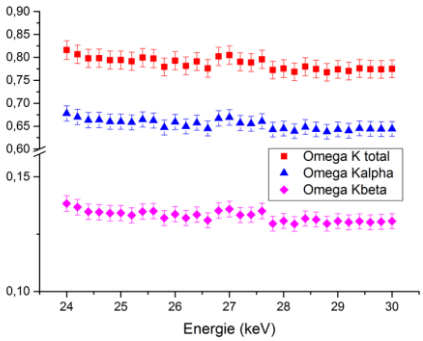

Fig. 6. ^{103m}Rh fluorescence yields results [5].

In addition, rhodium samples were activated in the ISIS experimental nuclear reactor facility at CEA Saclay to perform an absolute activity measurement by liquid scintillation counting using the Triple-to-Double Coincidence Ratio method, followed by X-ray spectrometry using a high-purity germanium detector to determine the photon emission intensities [10]. The new result (I_X = 0.0825) is derived with a significant reduction of the uncertainty.

As in the case of niobium, these experimental values are consistent with the other experimental data and close to the theoretical and semi-empirical values published in the last sixty years [5].

4 Conclusions and perspectives

In collaboration with LNHB and LARC CEA laboratories, LDCI has been engaged since ten years in an intensive work programme for improving the measurement of the activities of ^{93m}Nb and ^{103m}Rh X-Ray emitters. This work has led to several accomplishments such as some nuclear data re-evaluation with reduction of the associated uncertainties using an innovative combination of modelling codes and experiments.

However, to achieve a consistent set of data for these two dosimeters and to have a qualified measurement methodology, a significant amount of acquired data have to be analysed and some to be produced (accurate measurements of nuclear data using a bolometer device). Already published and oncoming results will be evaluated in the aim of their integration in the DDEP databases. The results will further enhance the certified measurement process at the MADERE facility.

In addition, studies are still ongoing on the modelling of the spectroscopy measurement devices in the aims to extend the X-Ray measurement techniques to different geometries and to other X-rays emitters.

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