

Retrospective Dosimetry based on the $^{93}\text{Nb}(n,n')^{93\text{m}}\text{Nb}$ reaction. Techniques applied at SCK•CEN.

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Under the contract of EU
contractnr. FIKS-CT-2000-91

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Abstract

RETROSPEC is a joint project of NRG Petten (The Netherlands), VTT Espoo (Finland) and SCK•CEN Mol (Belgium), sponsored by the European Commission. The aim of the project is to investigate the use of the $^{93}\text{Nb}(n,n')^{93\text{m}}\text{Nb}$ reaction for retrospective dosimetry. Retrospective dosimetry is in particular of importance for those reactors that do not have (well-established) surveillance programs for the reactor pressure vessel. Often this is the case for Eastern European type of reactors (VVER).

For this purpose, several materials representative for VVER reactor pressure vessel material were distributed amongst the partners of the project. Each partner developed its own technique to dissolve the material, separate niobium from the solution and determine the $^{93\text{m}}\text{Nb}$ specific activity. This report describes the techniques applied at SCK•CEN in order to accomplish this.

Table of contents

1. Introduction	6
2. Measurements and Results	8
2.1 Available materials	8
2.2 γ -spectrometry measurements of the steel specimen	8
2.3 Dissolution, isotope separation and mass determination	10
2.3.1 Dissolution of the samples.....	11
2.3.2 Chemical composition of the inactive samples	11
2.3.3 Separation procedure	11
2.3.4 ^{93}Nb mass determination	13
2.4 Target preparation and activity measurements	14
2.4.1 Niobium target preparation.....	14
2.4.2 $^{93\text{m}}\text{Nb}$ activity measurements.....	15
3. Discussion	18
4. Conclusion.....	20

1. Introduction

Reactor components and in particular the reactor pressure vessel sustain damage due to irradiation. This irradiation induced damage is mainly caused by interaction of fast neutrons with atoms of the metal lattice. In order to monitor the embrittlement of the reactor pressure vessel, most nuclear power plants have established specific surveillance programs. For this purpose, surveillance capsules equipped with neutron dosimeters and with material representative for reactor pressure vessel steel are developed and irradiated near the reactor pressure vessel.

In some Eastern European type of reactors (VVER), such surveillance programs are not (well) established. In order to deal with this lack of information, retrospective neutron dosimetry might be an alternative. Small amounts of structural material (1-100 mg) from operating nuclear power plants can be obtained using robotic tools during reactor shutdown periods. Neutron activation products in these samples can be determined using γ -spectrometry measurements, and several techniques to determine the elemental composition of the samples exist. If the reactor irradiation history is known, neutron fluences that were present at the sample positions during the nuclear power plant operation (until sample removal) can be determined.

An attractive isotope for this purpose is ^{93}Nb , which is present in the reactor pressure vessel cladding material ($\sim 1\%$) and in the pressure vessel steel as an impurity (~ 1 to 10 ppm). Thanks to the long half live of the $^{93}\text{Nb}(n,n')^{93\text{m}}\text{Nb}$ activation product (16.13 y [1]), the conversion from measured specific activity to neutron fluence is not strongly dependent on the reactor irradiation history. This reaction moreover has a suited threshold energy of 1 MeV.

The determination of the $^{93\text{m}}\text{Nb}$ specific activity is not straightforward, as it requires the detection of low-energy X-rays. First of all, the samples need to be dissolved in order to avoid too high X-ray self absorption. Secondly, niobium needs to be separated from the other elements. Especially ^{60}Co should be removed, which is highly present due to the big thermal $^{59}\text{Co}(n,\gamma)^{60}\text{Co}$ cross section, because its presence would hamper the detection of the $^{93\text{m}}\text{Nb}$ X-rays.

The RETROSPEC project aims at investigating the use of ^{93}Nb for retrospective dosimetry. It is a joint project of NRG Petten (The Netherlands), VTT Espoo (Finland) and SCK•CEN Mol (Belgium), sponsored by the European Commission (contract FIKS-CT-2000-91). Small pieces from four materials representative for VVER-type reactors were distributed amongst the three partners of the RETROSPEC project. Each partner followed its own procedure to:

- determine the neutron activation products in the steel specimen;
- dissolve the steel specimen and perform the isotope separation;
- determine the ^{93}Nb mass;
- determine the $^{93\text{m}}\text{Nb}$ specific activity.

This report describes the experimental approach of the SCK•CEN. Similar reports are provided by the other partners of the project [2-4]. Moreover, a general report with a detailed description of the RETROSPEC project and with an overview of all the techniques developed is available [5].

Chapter 2 provides a detailed description of the experimental techniques applied at the SCK•CEN and gives an overview of the results obtained from the measurements. It is subdivided in four parts. First, an overview of the available materials is given. The next three parts are in accordance with the three main steps that can be distinguished in the experimental procedure.

The obtained results are discussed in Chapter 3. The advantages and limitations of the applied techniques are deduced.

Chapter 4 briefly summarises the conclusions that can be drawn from this research.

2. Measurements and Results

This chapter gives an overview of the materials available for the measurements, the measuring techniques and the results that are obtained. Three main steps in the experimental procedure can be distinguished. In the first step, γ -spectrometry measurements are performed on the steel specimens. Secondly, the steel specimens are dissolved, ^{93}Nb is isolated and its mass determined. Finally, thin deposits are made from this solution that are used for the determination of the $^{93\text{m}}\text{Nb}$ specific activity.

2.1 Available materials

Four materials representative for reactor pressure vessel material in VVER-type reactors (base and cladding) have been selected for the investigation of the feasibility of retrospective dosimetry based on the $^{93}\text{Nb}(n,n')^{93\text{m}}\text{Nb}$ reaction. These materials are different in composition (amount of niobium in the material) and in elapsed time since the end of irradiation. Small pieces from the following materials were distributed amongst the partners from the RETROSPEC project. Also indicated are those samples that were sent to and analysed at the SCK•CEN:

- SS2 type material (cladding) cut from charpy V specimens that were irradiated in the 4th Dukovany Nuclear Power Plant (Czech Republic) during the 7th cycle in the period 1993-1994. Two samples, labeled 'B3' and 'C11', were analysed. In addition, one inactive sample labeled 'nr. 19' was used to test the chemical procedure. The niobium content is about 1 wt.%.
- Material from specimen 6K184 (cladding) irradiated in the 1st Loviisa Nuclear Power Plant (Finland) during cycles 10 to 13 in the period 1986-1990. It consists of two materials: outer layer containing about 1 wt.% niobium, labeled 'red', and inner layer containing much less niobium, labeled 'blue'. Two samples were analysed: 'red3' and 'blue3'. This material will be referred to as 'Loviisa old' in this report.
- Material from specimen 6K199 (cladding) that was irradiated in 1st Loviisa Nuclear Power Plant in the period 2000-2001. The niobium content is about 1 wt.%. This material will be referred to as 'Loviisa new' in this report. An inactive sample of the same composition (6K200, cut from the same material as and just next to 6K199) was used for chemical analyses.
- Material 15Kh2MFA (base) irradiated at the High Flux Reactor in Petten (Netherlands) for experiment LYRA-02 during cycles 9802-9805 in the period February 1998 - June 1998. Six samples were analysed: 'L125/1', 'L125/4', 'L127/1', 'L127/4', 'L129/1' and 'L129/4'. The niobium content is about 50 ppm.

For a detailed description of the materials is referred to [6].

2.2 γ -spectrometry measurements of the steel specimen

The γ -spectrometry measurements were performed by means of a high-purity Ge-detector coupled to a Canberra-Eurysis ADC. The Ge-detector was calibrated using a set of certified ^{152}Eu reference sources (from PTB). The γ -ray spectra were analysed with the Canberra-Eurysis software Genie 2000.

All samples were cut in pieces after the measurements. Measuring these pieces may provide information on the existence of neutron fluence gradients during the irradiation or on the

niobium distribution in the material. Information on fast neutrons can be obtained from ^{54}Mn , ^{60}Co and ^{94}Nb may give information on thermal and epithermal neutrons.

An overview of the results is given in Tables 1-4. All specific activities are expressed in Bq/g steel.

Table 1 presents the specific activities obtained from the 'Dukovany' material. Both samples 'B3' and 'C11' were cut in 2 pieces ('B3A', 'B3B' and 'C11A', 'C11B', respectively). The specific activities were calculated to the end of irradiation 14/09/1994, 06:00. The correction factors applied for γ -ray absorption in the steel are 1.054 for ^{54}Mn , 1.043 for ^{60}Co and 1.055 for ^{94}Nb . The uncertainties (1σ) on the specific activities are about 3 % for ^{60}Co and ^{54}Mn and 14 % for ^{94}Nb .

Table 1. Characteristics and specific activities – 'Dukovany' samples.

Identification	Mass [g]	Dimensions [mm]	Spec. Activity ^{54}Mn	Spec. Activity ^{60}Co	Spec. Activity ^{94}Nb
B3	0.6282	10.0 x 5.0 x 2.0	2.00E+07	1.45E+07	8.43E+03
C11	0.7042	10.0 x 5.0 x 2.0	1.93E+07	1.45E+07	8.54E+03
B3A	0.3099	4.8 x 5.0 x 2.0	1.97E+07	1.43E+07	7.99E+03
B3B	0.2760	4.4 x 5.0 x 2.0	1.76E+07	1.36E+07	6.17E+03
C11A	0.2895	4.5 x 5.0 x 2.0	1.87E+07	1.37E+07	7.46E+03
C11B	0.3667	5.0 x 5.0 x 2.0	1.72E+07	1.35E+07	6.67E+03

The specific activities obtained from the 'Loviisa old' material are summarised in Table 2. Again the samples were cut in 2 pieces. The specific activities were calculated to the end of irradiation 07/07/1990. The correction factor applied for γ -ray absorption in the steel is 1.032. No ^{54}Mn activity was observed. This is a consequence of its relatively short half live of 312.3 days [1] with respect to the cooling time of about 13 years. The uncertainty (1σ) on the specific activities is about 3 %.

Table 2. Characteristics and specific activities – 'Loviisa old' samples.

Identification	Mass [g]	Dimensions [mm]	Spec. Activity ^{60}Co
Red3	0.4748	13.6 x 1.5 x 3.1	1.21E+07
Blue3	0.4641	13.7 x 1.5 x 3.1	1.21E+07
Red3A	0.1800	5.0 x 1.5 x 3.1	1.20E+07
Red3B	0.2759	8.0 x 1.5 x 3.1	1.15E+07
Blue3A	0.2117	6.0 x 1.5 x 3.1	1.14E+07
Blue3B	0.2348	7.0 x 1.5 x 3.1	1.14E+07

Table 3 presents the specific activities obtained from the 'Loviisa new' material. The sample ('C2') was cut in 3 pieces. The specific activities at the end of irradiation (01/09/2001, 06:30) of ^{54}Mn and ^{60}Co were determined. The correction factors applied for γ -ray absorption in the steel are 1.064 and 1.081 for sample 'C2' and 1.043 and 1.054 for the subdivided parts for ^{54}Mn and ^{60}Co , respectively. The uncertainty (1σ) on the specific activities is about 3 %.

Table 3. Characteristics and specific activities – ‘Loviisa new’ samples.

Identification	Mass [g]	Dimensions [mm]	Spec. Activity ⁵⁴ Mn	Spec. Activity ⁶⁰ Co
C2	0.6576	4.0 x 3.0 x 7.0	4.39E+06	4.76E+06
C2A	0.1869	4.0 x 3.0 x 2.0	4.35E+06	4.82E+06
C2B	0.1838	4.0 x 3.0 x 2.0	4.37E+06	4.75E+06
C2C	0.1761	4.0 x 3.0 x 2.0	4.37E+06	4.70E+06

The specific activities at the end of irradiation (01/06/1998) obtained from the ‘Lyra’ samples are shown in Table 4. The correction factors applied for γ -ray absorption in the steel are 1.064 for ⁵⁴Mn and 1.081 for ⁶⁰Co. The uncertainties (1σ) on the specific activities are about 3 %.

Table 4. Characteristics and specific activities – ‘Lyra’ samples.

Sample	Mass [g]	Dimensions [mm]	Spec. Activity ⁵⁴ Mn	Spec. Activity ⁶⁰ Co
L 125/1	0.3911	4.3 x 4.0 x 3.0	9.14E+06	3.20E+05
L 125/4	0.3987	4.3 x 4.0 x 3.0	1.15E+07	4.54E+05
L 127/1	0.3809	4.3 x 4.0 x 3.0	9.12E+06	3.30E+05
L 127/4	0.3817	4.2 x 4.0 x 3.0	1.15E+07	4.59E+05
L 129/1	0.3919	4.3 x 4.0 x 3.0	9.65E+06	3.31E+05
L 129/4	0.3899	4.2 x 4.0 x 3.0	1.23E+07	4.61E+05

2.3 Dissolution, isotope separation and mass determination

The applied dissolution and isotope separation procedures were developed and optimised using a representative inactive reactor vessel material (‘Dukovany n°19’), containing approximately 1 wt.% of niobium.

A first dissolution attempt was made using a mixture of aqua regia (HCl/HNO₃: 3/1) and hydrofluoric acid. The mixture was heated in a Teflon beaker (<100°C). However the reaction was slow and did not result in a complete dissolution.

A second test was carried out in a microwave oven, in a closed Teflon pressure vessel and using a mixture of hydrochloric, nitric and hydrofluoric acid, at a temperature of 200°C. This resulted in a clear solution; therefore this procedure was used for the dissolution of all samples within the project.

The solution of the inactive sample was used to test three different separation procedures, all making use of hydrofluoric acid in combination with hydrochloric or nitric acid as eluents.

Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) was used to evaluate the quality of the procedures used to separate Nb from the matrix, giving special attention to certain elements of which radionuclides are formed during the reactor pressure vessel exposure as a result of neutron activation.

To achieve this, the raw dissolution of reactor vessel material was analysed, followed by the different separation fractions of the three methods used. For all fractions a blank of the eluent was measured. A yield was calculated, relative to the amount found in the dissolved vessel sample.

One separation method was discarded because the niobium was spread out over several fractions, and it also used the most corrosive eluents. For the two remaining separation methods results were similar, therefore the one already frequently used in this laboratory for the separation of niobium was chosen to be used on the active samples of the project.

2.3.1 Dissolution of the samples

From each sample, approximately 300 mg of material was dissolved in a mixture of HCl/HNO₃/HF in a ratio of 5/1/1. The mixture was put in a closed teflon pressure vessel in a microwave oven. The oven was programmed and controlled to raise the temperature to 200°C in 9 minutes, keeping it subsequently at this temperature for 11 minutes. After transfer and rinsing this resulted in about 30 g of raw solution.

2.3.2 Chemical composition of the inactive samples

The chemical composition of the inactive samples 'Dukovany n°19' and Loviisa '6K200' was determined by ICP-MS. The results, expressed in units of wt.% in the steel, are presented in Table 5.

Table 5. Chemical composition of the inactive samples.

Sample	Nb	Fe	Cr	Ni	Mn	Co
Dukovany n°19	0.79	67.4	17.9	10.1	1.47	0.02
Loviisa 6K200	0.57	69.2	17.8	9.25	1.26	0.02

2.3.3 Separation procedure

After dissolution an amount of raw solution, corresponding to approximately 50 mg of reactor vessel material, was run through 2 isotope separation steps:

First step: column I:

- Conversion of the sample to 1M HF/0.05M HNO₃
- Application on a column filled with 1-2g Dowex 1-X8
- Washing of the column with 1M HF/0.05M HNO₃
- Elution of Nb from the column with 1M HF/4M HNO₃

Second step: column II:

- Conversion of (part of) the eluent of column I to 3M HCl/20% HF
- Application on a column filled with 2g Dowex 1-X8
- Washing of the column with 3M HCl/20% HF
- Elution of Nb from the column with 3M HCl/0.05M HF

Part of the eluent of column II was converted to 1M HF. This solution was then used to perform mass determination of ⁹³Nb and activity measurements of ^{93m}Nb.

For some samples these separation steps were monitored by γ -spectrometry, using high purity Ge-detectors connected to the necessary electronics. ⁹⁴Nb, that emits two strong γ -photons, was used as tracer. Analyses of the recorded γ -spectra were carried out using the GENIE 2000 software from Canberra-Eurysis. The detectors were calibrated for energy and efficiency using a standard source prepared from a certified mixed γ -standardised solution containing 10 different radionuclides with γ -energies ranging from 60 keV to 1836 keV.

The results, expressed in Bq/g steel, are presented in Table 6. As it makes no sense at this stage to calculate the activities at their respective end of irradiation dates, these decay corrections are not done. Instead, all activities given in Table 6 are those at the time of measurement.

Table 6. Overview of the isotope separation steps.

Sample	Starting material		Column I		Column II	
	⁹⁴ Nb	Interfering γ -emitters	⁹⁴ Nb recovered	Interfering γ -emitters	⁹⁴ Nb recovered	Interfering γ -emitters
Red 3A	6.68E+03	⁶⁰ Co: 2.43E+06	6.27E+03 (94%)	⁶⁰ Co: 14	-	-
Blue 3A	< 600	⁶⁰ Co: 2.26E+06	28	⁶⁰ Co: < 10	-	-
B3A	8.2E+03	⁵⁴ Mn: 2.3E+06 ⁶⁰ Co: 4.88E+06	7.40E+03 (90%)	⁵⁴ Mn: <15 ⁶⁰ Co: 28 ¹²⁵ Sb: 550	7.39E+03 (90%)	⁶⁰ Co: < 18 ¹²⁵ Sb: < 100
C11A	8.8E+03	⁵⁴ Mn: 2.0E+06 ⁶⁰ Co: 4.64E+06	6.5E+03 (74%)	⁵⁴ Mn: <13 ⁶⁰ Co: < 10 ¹²⁵ Sb: 541	6.6E+03 (75%)	¹²⁵ Sb: < 85
C2	2.4E+03	⁵¹ Cr: 3.3E+04 ⁵⁴ Mn: 1.95E+06 ⁵⁷ Co: 1.76E+04 ⁵⁸ Co: 4.34E+05 ⁵⁹ Fe: 3.0E+04 ⁶⁰ Co: 4.18E+06 ⁷⁵ Se: 4.6E+03 ¹⁰⁹ Cd: 6.2E+04 ¹²⁴ Sb: 2.7E+03 ¹⁸² Ta: 7.9E+04 ¹⁹² Ir: 1.5E+03	2.38E+03 (99%)	⁵¹ Cr: <400 ⁵⁴ Mn: 29 ⁵⁷ Co: <13 ⁶⁰ Co: <20 ⁷⁵ Se: 36 ¹⁰⁹ Cd: 360 ^{110m} Ag: 3.62E+03 ¹¹³ Sn: 320 ¹²⁴ Sb: 2.4E+03 ¹²⁵ Sb: 530 ¹⁸² Ta: 790 ¹⁹² Ir: 1.68E+03	2.28E+03 (95%)	⁵¹ Cr: <12 ⁵⁴ Mn: <12 ⁵⁷ Co: <13 ⁶⁰ Co: <7 ⁷⁵ Se: <15 ¹⁰⁹ Cd: 30 ^{110m} Ag: <17 ¹¹³ Sn: <17 ¹²⁴ Sb: 24 ¹²⁵ Sb: <40 ¹⁸² Ta: <30 ¹⁹² Ir: 69

The results show that the decontamination of ⁶⁰Co and ⁵⁴Mn is already very high from the first column. Whereas in the untreated sample ⁹⁴Nb represented for example 0.03 % (sample 'C2') of the total γ -activity, in the eluent of column I this has already increased to 20 %, with an excellent recovery of ⁹⁴Nb. However, other previously masked γ -emitters now become visible in the spectrum, necessitating the second separation step.

γ -spectrometry monitoring of the final conversion of the eluent of column II tot 1M HF revealed a quantitative recovery of ⁹⁴Nb (100 %). In general the second column separation is only necessary for reactor vessel samples that had a short cooling period (elapsed time between end of irradiation and analyses). This is the case for sample 'C2', where most of the radionuclides detected after column I have a half-life < 1 year. For older samples the first column separation is more than adequate for the preparation of a deposit for the activity measurements of ^{93m}Nb.

2.3.4 ^{93}Nb mass determination

Measurement of the ^{93}Nb content was performed using Inductively Coupled Plasma - Mass Spectrometry (ICP-MS), using a VG Plasmaquad PQ3N. The sample introduction part of the instrument is fitted within a glove box, permitting the measurement of radioactive samples. Calibration of the instrument was based on a Nb standard solution, as control standard a Spex multi-element standard was used. ^{103}Rh was used as internal standard.

ICP-MS measurements were done on the raw solutions, on the eluents of column II and on the 1M HF solutions.

From the results for the raw solutions, the ^{93}Nb content of the steel samples could be calculated. These values are presented in Table 7.

Table 7. ^{93}Nb content of the steel samples.

Sample	Sub sample	mg ^{93}Nb /g steel
Dukovany	B3A	6.0
	B3B	8.3
	C11A	8.0
	C11B	8.1
Loviisa old	Red3A	8.4
	Red3B	8.5
	Blue3A	0.036
	Blue3B	0.050
Loviisa new	C2	7.8
Lyra-02	125/1	0.003
	125/4	0.003
	127/1	0.003
	127/4	0.002
	129/1	0.002
	129/4	0.002

Based on the results for the raw and the HF solutions, the overall recovery of ^{93}Nb for the whole separation and conversion process was calculated, resulting in about 90 % on average. This however is not of crucial importance, as the specific $^{93\text{m}}\text{Nb}$ activity will be calculated from the ^{93}Nb mass determination and the $^{93\text{m}}\text{Nb}$ activity, both measured on the same 1M HF solution.

The mass determination results for the 1M HF solutions are presented in Table 8.

Table 8. ^{93}Nb content in the 1 M HF solutions.

Sample	Sub sample	$\mu\text{g } ^{93}\text{Nb/g 1M HF solution}$
Dukovany	B3A	76.39
	B3B	65.21
	C11A	74.91
	C11B	48.86
Loviisa old	Red3A	80.88
	Red3B	74.91
	Blue3A	0.50
	Blue3B	0.34
Loviisa new	C2	64.93

The overall uncertainty on these results is about 5 % (1σ), except for the 'blue' samples, where an uncertainty of 10 % (1σ) is estimated.

The 'Lyra' samples are only measured as raw solutions because their niobium content is even 10 times lower than the 'blue' samples, which were already too low for $^{93\text{m}}\text{Nb}$ activity measurements.

The detection limit for ^{93}Nb is 1 $\mu\text{g/l}$. Since overall recovery of Nb is very good, it can be calculated that a minimum amount of niobium in a reactor vessel steel sample of about 50 $\mu\text{g/g}$ is necessary in order for an accurate measurement of the 1M HF solution to be possible.

2.4 Target preparation and activity measurements

The experimental procedure applied for the niobium target preparation and the $^{93\text{m}}\text{Nb}$ activity measurements is mainly based on techniques formerly developed at SCK•CEN (see e.g. [7,8] and references therein) and elsewhere (see e.g. [9]). Applying these same techniques moreover has the advantage that suited $^{93\text{m}}\text{Nb}$ calibration samples are available. Indeed, for the purpose of an intercomparison of $^{93\text{m}}\text{Nb}$ K X-ray emission probabilities in 1985 [10], a $^{93\text{m}}\text{Nb}$ solution was standardised at IRMM (former CBNM) using liquid scintillation (see certificate in Appendix 1). From this solution, five deposits were prepared for the intercomparison, which were through this intercomparison proven to be suitable calibration samples for absolute $^{93\text{m}}\text{Nb}$ activity measurements.

2.4.1 Niobium target preparation

In order to strongly reduce X-ray self-absorption in niobium dosimeters, a method for preparing thin niobium deposits was developed in the late 1970s (see [7-9] and references therein). The niobium wire or foil was dissolved; a few drops from this solution were brought on a filter paper tissue and afterwards covered with a thin layer of plastic. In this way, X-ray self-absorption was reduced to less than 1 %.

The target preparation procedure for the samples of the RETROSPEC project is based on this technique:

- The solution containing the niobium is sucked up in a small polyethylene bottle. This bottle has a very small entrance to avoid evaporation of the solution and to allow making small drops for the target preparation.
- A few drops of the solution (~ 20 to 60 μg solution) are brought on a filter paper tissue (13 mm diameter, ~ 8 $\text{mg}\cdot\text{cm}^{-2}$ thickness) supported on a thin aluminium disc.

- The polyethylene bottle is accurately weighed before and after the drops are brought on the filter paper. This differential weighing allows to determine the amount of solution on the filter paper with an uncertainty of about 0.1 %.
- After a drying period of about two hours a thin plastic layer is sprayed on the deposit. This is done to protect the niobium deposit from mass loss. Also, this plastic layer prevents curling of the paper and provides adhesive power between the paper tissue and the support. Concerning the latter two considerations, additionally to cover the deposit with a plastic layer, a thin double-sided adhesive tape can be used to fix the filter paper on the aluminium support, before the solution is brought on the filter paper.

The previously mentioned ^{93m}Nb calibration deposits were prepared in the same way, using the certified 1 M HF / 1 M HNO₃ solution. In this way, it was possible to perform the measurements and the efficiency calibration under exactly the same detection geometry. From each solution of the RETROSPEC samples, at least two deposits were prepared.

2.4.2 ^{93m}Nb activity measurements

The ^{93m}Nb X-rays (K_{α} : 16.52-16.62 keV and K_{β} : 18.61-18.95 keV [1]) were detected by means of a planar Low Energy Ge-detector coupled to a Canberra-Eurysis ADC. The efficiency calibration of this Low Energy Ge-detector was done using the above-mentioned set of ^{93m}Nb deposits with an uncertainty of about 2 %. In view of the low count rates, only the K_{α} X-rays were used for the analyses.

A typical spectrum obtained from one of the samples is shown in Figure 1. This figure clearly shows that a very 'clean' integration of the K_{α} X-ray peak was possible. About 6500 counts were detected in the K_{α} peak after about 40 hours of data taking. Separate background measurements were performed to ensure that no contaminant γ -ray or X-ray contributions were present in this energy region. An additional verification of a correct K_{α} X-ray detection was done by comparing the observed K_{α}/K_{β} ratio with the known X-ray emission probabilities [1].

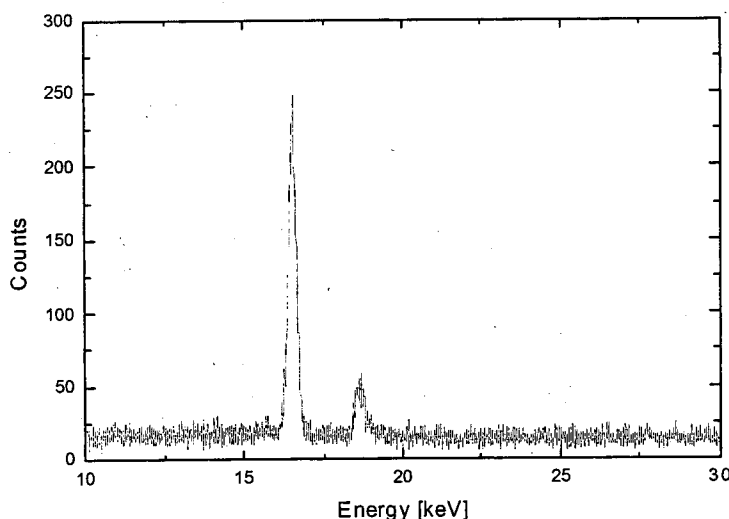


Figure 1. Spectrum showing the ^{93m}Nb K X-rays.

An overview of the obtained results for all materials is presented in Tables 9-12. The ^{93m}Nb specific activities are expressed in Bq/g ^{93m}Nb .

Table 9 and Table 10 present the results obtained from the 'Dukovany' material. Both parts of both materials 'B3' and 'C11' were brought into separate solutions and several deposits from each solution were prepared. The amount of ^{93}Nb and the measured $^{93\text{m}}\text{Nb}$ specific activities are summarised in the tables. The average specific activities for 'B3A' and 'B3B' are $6.07\text{E}+07$ Bq/g and $6.92\text{E}+07$ Bq/g, respectively.

Three deposits were prepared from solution 'C11A'. The mutual agreement between these results is not very good. This is explained by the fact that some problems (mainly due to poor adhesion between aluminium backing and filter paper) were encountered during the target preparation. The poor quality of these samples remains visible after the drying period. No new samples were prepared from this solution within the framework of this project. The average $^{93\text{m}}\text{Nb}$ specific activity obtained is $5.71\text{E}+07$ Bq/g. A more conservative uncertainty should be adopted.

Two deposits were prepared from solution 'C11B'. The average $^{93\text{m}}\text{Nb}$ specific activity is $6.92\text{E}+07$ Bq/g.

Table 9. $^{93\text{m}}\text{Nb}$ specific activities - 'Dukovany' material (a).

B3A		B3B	
^{93}Nb mass [μg]	$^{93\text{m}}\text{Nb}$ spec. activity	^{93}Nb mass [μg]	$^{93\text{m}}\text{Nb}$ spec. activity
1.54	$5.88\text{E}+07$	1.62	$6.92\text{E}+07$
1.79	$6.16\text{E}+07$	1.65	$6.92\text{E}+07$
2.30	$6.19\text{E}+07$	1.93	$6.93\text{E}+07$
3.12	$6.02\text{E}+07$		
3.92	$6.08\text{E}+07$		
	$\langle A \rangle = 6.07+07$		$\langle A \rangle = 6.92+07$

Table 10. $^{93\text{m}}\text{Nb}$ specific activities - 'Dukovany' material (b).

C11A		C11B	
^{93}Nb mass [μg]	$^{93\text{m}}\text{Nb}$ spec. activity	^{93}Nb mass [μg]	$^{93\text{m}}\text{Nb}$ spec. activity
1.99	$5.70\text{E}+07$	1.22	$6.21\text{E}+07$
2.10	$5.90\text{E}+07$	1.16	$6.37\text{E}+07$
1.74	$5.53\text{E}+07$		
	$\langle A \rangle = 5.71\text{E}+07$		$\langle A \rangle = 6.29\text{E}+07$

The $^{93\text{m}}\text{Nb}$ specific activities obtained from the 'Loviisa old' material are summarised in Table 11. Two deposits were prepared from each solution of the 'Red3' material, yielding $3.51\text{E}+07$ Bq/g and $3.34\text{E}+07$ Bq/g for parts 'Red3A' and 'Red3B', respectively.

One deposit was prepared from the 'Blue3A' solution. The $^{93\text{m}}\text{Nb}$ specific activity on this deposit could not be determined, as no X-rays were detected. This is not surprising, as the ^{93}Nb content in the latter material is very low.

Table 11. ^{93m}Nb specific activities - 'Loviisa old' material.

Red3A		Red3B	
^{93}Nb mass [μg]	^{93m}Nb spec. activity	^{93}Nb mass [μg]	^{93m}Nb spec. activity
2.97	3.48E+07	2.57	3.21E+07
3.00	3.54E+07	2.48	3.47E+07
	<A> = 3.51E+07		<A> = 3.34E+07

Only one solution was prepared from the 'Loviisa new' material. The average specific activity resulting from the measurements of three deposits of this solution yields 1.87E+07 Bq/g. These results are presented in Table 12.

Table 12. ^{93m}Nb specific activities - 'Loviisa new' material.

C	
^{93}Nb mass [μg]	^{93m}Nb spec. activity
1.91	1.89E+07
2.60	1.82E+07
4.45	1.89E+07
	<A> = 1.87E+07

No attempt was undertaken to measure the ^{93m}Nb activity of the 'Lyra' material, as from the ICP-MS measurements it appeared that these samples contain even less niobium than the 'Loviisa old blue' material.

A realistic estimation of the uncertainty on the specific activities is summarised in Table 13. Estimated contributions to the uncertainty on the ^{93m}Nb specific activities. Table 13. The uncertainties on the ^{93}Nb mass and on the K_{α} X-ray peak area are combined quadratically, the result of which is added procentually to the systematic uncertainties (efficiency calibration, ^{93m}Nb decay constant). This results in an overall 1σ uncertainty on the specific activities of about 8 %. In reality the uncertainties on the K_{α} X-ray peak area vary from 2 % to 4 % for the different measurements. As it is not of importance for the purpose of this work, this was not taken into account when calculating the average specific activities in Tables 9-12. Instead of making a weighted average, an average uncertainty on the K_{α} X-ray peak area of 3 % was adopted.

Table 13. Estimated contributions to the uncertainty on the ^{93m}Nb specific activities.

Contribution	1σ uncertainty
Efficiency calibration	2 %
^{93}Nb mass determination in solution	5 %
Mass determination on deposit	0.1 %
^{93m}Nb decay constant	0.1 %
K_{α} peak area	3 %

3. Discussion

Dissolution tests indicate that reactor vessel samples are preferentially dissolved in a mixture of HCL/HNO₃/HF using a microwave oven. Different isotope separation procedures were tested and proven to be adequate; here the choice was based on practical considerations (less corrosive eluents, experience with the procedure). For reactor vessel samples that had only a short cooling period prior to analysis a second separation step was needed.

Mass determinations were performed by means of ICP-MS, yielding an overall uncertainty of 5 %. Based on a detection limit of about 1 µg ⁹³Nb/l, it was calculated that for an accurate mass determination a minimum niobium content of the reactor vessel steel sample of about 50 µg/g is needed. This however is not the limiting step in the procedure to determine the ^{93m}Nb specific activity of the steel samples, as is explained further on.

Activity measurements (⁶⁰Co, ⁵⁴Mn, ⁹⁴Nb) were performed on steel specimen from all the distributed materials. In addition, the ^{93m}Nb activity from most of the materials could be determined. All these results agree well with the results obtained by the other partners from material that was subject to similar irradiation conditions [2-5].

The ⁹⁴Nb activity was only determined for the 'Dukovany' samples. Due to the very long half live of ⁹⁴Nb (2.03E+04 y [1]), this activity is very low, necessitating very long γ -spectrometry measurements. As it was not the scope of this project to determine ⁹⁴Nb activities, this was not done for the other materials.

The overall 1 σ uncertainty on the ^{93m}Nb specific activities is about 8 %. It is advised to make 3 to 5 samples from each solution. In this way, when adopting suited counting periods, the uncertainty on the K α X-ray peak area determination can become smaller than 2 %, which would result in an overall 1 σ uncertainty on the ^{93m}Nb specific activities of about 7 %. In case anomalously deviating results are obtained from samples from the same solution, a visual verification of the quality of these samples should be performed. If an anomaly on a sample is observed, the result from such a sample should be rejected.

From all the activities presented in Tables 1-4 and 9-12, no definite conclusions can be drawn on the existence of neutron fluence gradients, nor on the homogeneity of the niobium distribution in the material. As all the activities of the subdivided parts agree within the quoted uncertainties, the gradients or inhomogeneous distributions were small or not present at all.

The limiting step in the experimental procedure to determine ^{93m}Nb specific activities lies in the target preparation and γ -spectrometry measurement technique. Only amounts of the order of 0.05 g of solution can be brought on the filter paper (in order to prevent saturation and other disturbing effects), which corresponds to a few µg of ⁹³Nb for materials that contain about 1 % of niobium deposit. Therefore, the outlined technique for niobium target preparation and γ -spectrometry measurements should only be adopted for materials containing at least ~ 1 % of niobium.

Some improvements could be made to increase the K α X-ray count rate, e.g., using bigger filter paper or making the niobium concentration of the solution higher. This however would result in slightly bigger uncertainties; moreover the minimum required niobium content of the steel would not drastically change.

The advantage however of using these low quantities of solution is that very accurate K_{α} X-ray measurements are possible (see Figure 1). When measuring bigger quantities of material, even if an analogous standard source is available, scattering and absorption effects can always introduce additional uncertainties.

4. Conclusion

An experimental procedure to perform retrospective dosimetry based on the $^{93}\text{Nb}(n,n')^{93\text{m}}\text{Nb}$ reaction was developed and tested. Several steel specimens different in composition and in irradiation history were analysed. The $^{93\text{m}}\text{Nb}$ specific activities from the samples containing at least about 1 % niobium could be determined with an uncertainty of about 7-8 %. For materials with a lower niobium content, it is advised to adopt different target preparation and γ -spectrometry measurement techniques.

This method can be applied at institutes with a nuclear chemistry laboratory, disposing of an ICP-MS device, and with a γ -spectrometry laboratory, disposing of a suited Ge-detector.

REFERENCES

- [1]. WWW Table of Radioactive Isotopes, <http://ie.lbl.gov/toi/>.
- [2]. J. R. W. Woittiez, B. Beemsterboer and O. Zwaagstra, 'Retrospec: Radioactive vessel steel: Separation of Nb and Mn from Co and determination of the Nb content - Contribution of NAMS', NRG report K5160/03.53122/I, April 2003.
- [3]. W. P. Voorbraak, J. K. Aaldijk and J. R. W. Woittiez, 'Retrospective dosimetry of fast neutrons focussed on the reactions $^{93}\text{Nb}(n,n')^{93\text{m}}\text{Nb}$ and $^{54}\text{Fe}(n,p)^{54}\text{Mn}$ - Contribution of NRG', NRG report 20576/03.53535/C, May 2003.
- [4]. T. Serén and T. Kekki, 'Retrospective Dosimetry based on Niobium Extraction and Counting - VTT's contribution to the RETROSPEC project', VTT Research Notes 2203, Espoo, 2003.
- [5]. W. P. Voorbraak, T. Kekki, T. Serén, M. Van Bockstaele, J. Wagemans and J. R. W. Woittiez, 'Retrospective Dosimetry of fast neutrons focussed on the reaction $^{93}\text{Nb}(n,n')^{93\text{m}}\text{Nb}$ ', NRG report 20576/03.53641/P, May 2003.
- [6]. W. P. Voorbraak, 'RETROSPEC - Selection of materials', NRG report 20576/02.48664/I, March 2002.
- [7]. H. Tourwé and N. Maene, 'Fast neutron fluence measurements with the Nb-93(n,n')Nb-93m reaction and the application to long-term irradiations', Proc. 3rd ASTM-Euratom Symposium on Reactor Dosimetry, Ispra (1979).
- [8]. H. Tourwé *et al.*, 'Niobium Dosimetry Intercomparison in EBR II and BR2', Proc. 4th ASTM-Euratom Symposium on Reactor Dosimetry, Gaitersburg (1982).
- [9]. F. Hegedüs, 'Fast neutron dosimetry by the reaction $^{93}\text{Nb}(n,n')$. Counting technique for ^{93}Nb activity.', Proc. 2nd ASTM-Euratom Symposium on Reactor Dosimetry, Palo Alto (1977).
- [10]. P. D'hondt, Nb-93(n,n')Nb-93m measuring method, revised on basis of the DAVIS-BESSE intercomparison exercise, SCK•CEN report R-3152 (1997).

9