Journal of Nuclear Materials 377 (2008) 213–218

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

SIMS investigation of the spallation and transmutation products production in lead

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A B S T R A C T

The production of spallation and activation products in liquid metals (Pb or Pb–Bi) is an important issue in the frame of the MEGAPIE and other ADS studies. Although it is usually evaluated by well established codes like the MCNPX, experimental validations of the calculations in real conditions are rare. This work is an attempt to deliver experimental data using the material irradiated in the Swiss Spallation source (SINQ). A target composed of SS316L cladding tubes filled with Pb was irradiated in SINQ with a total proton charge of 10.03 Ah. A cross-section of one rod has been prepared for analysis in the PSI fully shielded secondary ion mass spectrometer (SIMS). Mass scans have been realized on one irradiated specimen and compared to a reference un-irradiated sample. The SIMS measurement delivers no absolute quantitative measurements but allow the determination of the mass distribution of the long lived spallation and activation products in real materials. The analysis shows the production of a raw of isotopes in the mass range 50–140 amu in agreement with calculation realized in model cases. The measurements across the specimen demonstrate also the homogeneity of the spallation and activation products content in the rod cross-section. This analysis provides useful information on the long lived isotopes production in lead based spallation targets like MEGAPIE.

1. Introduction

Advanced high power spallation targets such as MEGAPIE (Mega Watt Pilot Experiment) and that of the future accelerator driven system (ADS) devices utilize liquid Pb or Pb–Bi eutectic as target materials. Although using liquid metals can avoid problems like radiation damage in solid materials produced by high energy protons and spallation neutrons, the transmutation products in the liquid Pb or Pb–Bi can cause some other problems. For example, they may precipitate on the surfaces of solid structural materials and increase the corrosion effects or they may evaporate from liquid metals and cause serious contamination. Therefore, it is very important to precisely evaluate the quantity of the transmutation products, particularly the radioactive volatile elements such as Polonium, Mercury, Iodine, Krypton, Tritium, etc. Although such an evaluation can be done using a number of well established codes such as the MCNPX and FLUKA codes, experimental validations of the calculations are normally necessary as the calculated values are often too much either overestimated or underestimated.

Swiss spallation neutron source (SINQ) targets are usually composed of SS316-cladding-Pb rods [1]. In these target rods, the temperature of the Pb rods is normally below 300 °C. Therefore, it is believed that the most of the volatile elements are still contained in Pb. Since the proton and neutron fluences of each target rod can be relatively precisely calculated, it is possible to obtain precise production cross-sections if the transmutation elements can be precisely measured. In this campaign, different analytical methodologies such as gamma spectrometry, secondary ion mass spectrometry (SIMS), inductive coupled plasma mass spectrometer (ICPMS) and radiochemistry analyses have been applied. In the present paper, the results of SIMS analysis are presented.

2. Experimental

2.1. Specimen

A small disc of about 2 mm thickness was cut from the target rod of SINQ Target-4, which received the maximum proton fluence ($\sim 5.5 \times 10^{25}$ m^{-2}) in this target. The detailed information of the irradiation can be found in [1].

The lead composition before irradiation is given in Table 1 for the elements with concentrations larger than 20 ppm (other than Fe).

The accumulated dose profile along the rod shows a Gaussian like distribution with a sigma of about 22 mm. A 19 mm thick cross-section has been cut in the rod at about 25 mm out of the peak intensity. The accumulated proton dose in the specimen was about 3.1×10^{25} m^{-2}, the neutron dose about 7.5×10^{25} m^{-2} at an irradiation temperature of about 250 °C. The accumulated dose in the steel cladding was about 11 dpa. The steel cladding of the lead rod has an inner diameter of 9.6 mm. The internal volume

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doi:10.1016/j.jnucmat.2008.02.086

Table 1
Concentration of the trace elements in the Pb before irradiation

Element concentration (ppm)										
Na	P	S	Fe	Cu	Ge	Ag	Sn	Sb	Pb	Bi
56	23	25	15	462	27	45	136	989	Main	224

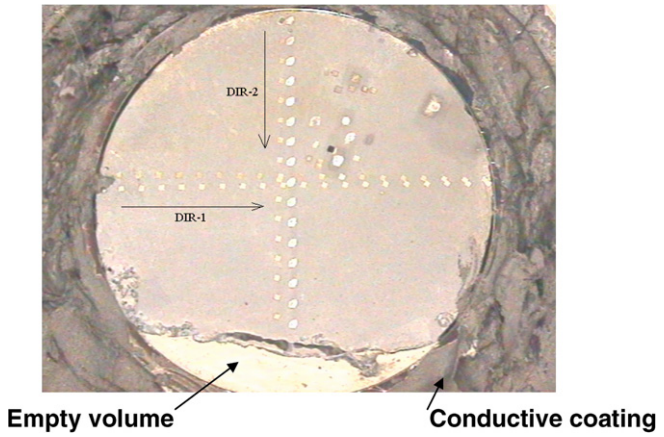

Fig. 1. Macrograph of the reference specimen R1 after measurements. The direction of the line-scans are given on the picture. The horizontal lead piece diameter is 9.6 mm.

is only partially filled with solid lead at room temperature in order to accommodate for the thermal expansion and gas (H, He, etc.) release occurring during irradiation.

The sample was embedded in epoxy resin grinded down and polished using a standard metallographic procedure. A reference, non-irradiated, sample (R1) was extracted from a spare rod and prepared using the same procedure.

In order to avoid surface charging effects, the Pb–Bi material was electrically connected to the SIMS specimen holder with conductive coating (Fig. 1).

2.2. Experimental procedure

Secondary ion mass spectrometry (SIMS) allows the determination of isotopic relative content of trace elements (down to ppm level) in solid materials [2]. A quantification of the acquired data is difficult and has not been realized in this study. However, isotopic ratio calculation gives semi-quantitative information on the material composition.

Due to the very high radioactivity of the irradiated material, the two specimens have been investigated with the fully shielded ATOMIKA-4000 SIMS of the PSI hot laboratory. An O_2^+ primary ion beam has been used with a current between 150 and 850 nA.

Mass scans (MS) were carried out on both samples in order to determine which isotopes are present in the materials and their ratios. The isotope distribution in the Pb disc was determined using the line-scans (LS) method across two perpendicular directions.

The isotopes count rates are given in counts per second (cps). The obtained count rates have been normalized with the beam current in order to get a result independent from the primary beam intensity.

The measurements on the irradiated specimen are compared to the analyses on the un-irradiated reference material.

3. Measurements

3.1. Mass scans

Mass scans have been realized at different positions on the specimens. They allow the determination of the activation products list created in detectable concentration in the specimen. The comparison between the reference specimen and the irradiated one allows excluding impurities present in the original material. Based on the results of the mass scans, 12 isotopes were chosen for the analysis of their distribution across the specimen (line-scan setup).

The baselines or background level in the mass scans (MS) were estimated to 10 cps for all masses. The machine parameters for the MS on both samples were optimized for the isotope ^{208}Pb. Typical complete MS acquired in both specimens are presented in Fig. 2.

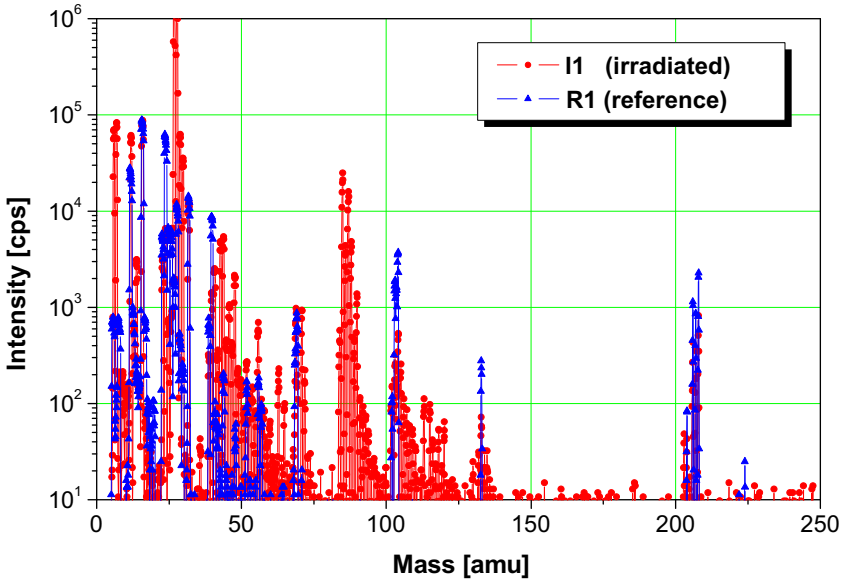

Fig. 2. Mass scans comparison between both specimens (overview).

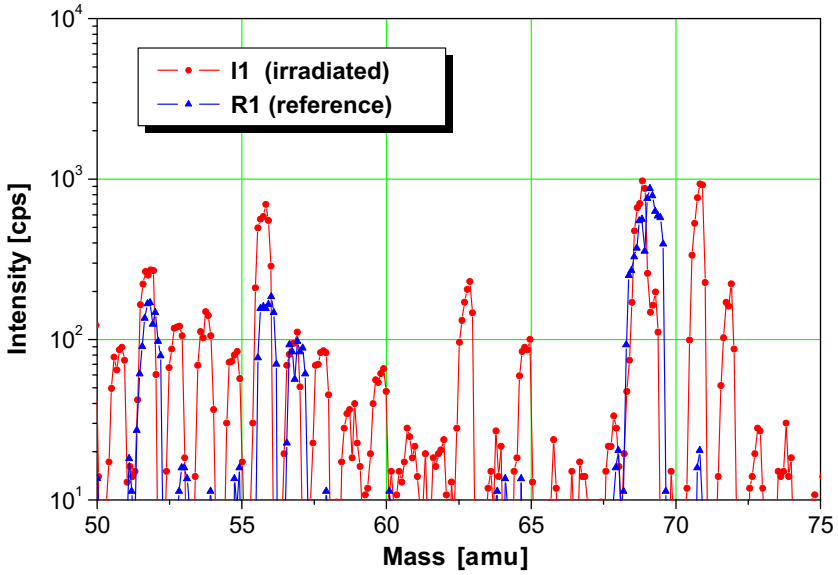

Fig. 3. Mass scans comparison between both specimens in range 50–75 amu.

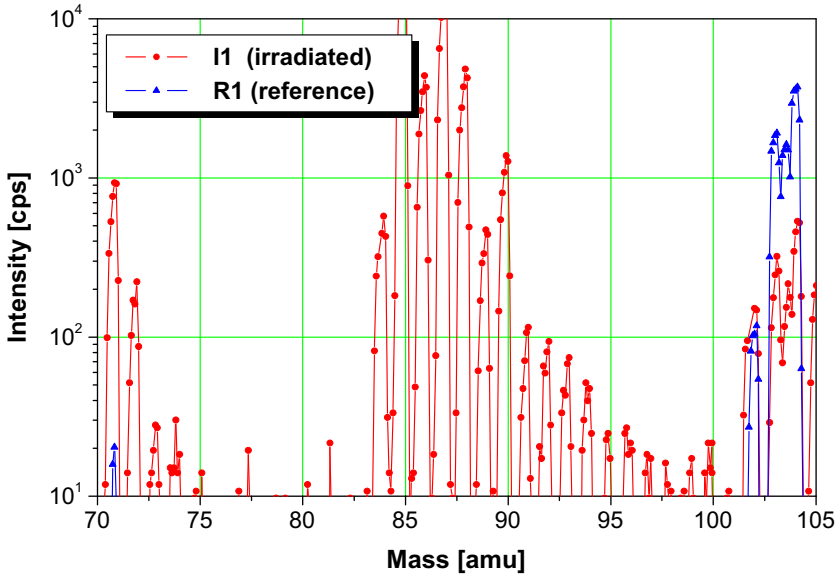

Fig. 4. Mass scans comparison between both specimens in range 70–105 amu.

Tacking account the different ionization probabilities the isotopes detected in the un-irradiated specimen correspond to the trace elements present in the original material (Table 1) or to known surface contaminant.

The complete MS show that some isotopes are present only in the irradiated specimen I1, for example, in range 80–100 amu and 105–130 amu. This confirms that SIMS is sensitive enough to detect spallation and activation products in Pb–Bi.

Detail analyses of the MS show that the isotopes present in the reference specimen are also found in the irradiated material with a similar or higher intensity. Typical example is given in Fig. 3 for the mass range 50–75 amu.

For some light masses (20, 24, 40) a higher signal is recorded in the reference material. This is very probably due to local variation of the contaminant content in the original material or on the surface of the specimens.

The presence of new isotopes created during irradiation is very clear in mass range 70–100 amu as it can be seen in Fig. 4. The mass range is representative for single loaded ions of Kr, Rb, Sr, Y, Zr, Nb and Mo created by spallation or activation processes.

The mass range 100–105 amu corresponds to a mix of the double loaded Pb and Bi isotopes, explaining the strong signal in the reference specimen, and some spallation or activation products.

Finally another clear production of spallation and activation products are detected in the mass range 105–140 (Fig. 5) corresponding to isotopes of Pd, Ag, Sn, Ba. The peak observed at 133 amu is an artifact due to the contamination of the vacuum chamber with Cs used as primary ion in other investigations.

The mass range 200–220 amu including the Pb and Bi single charged isotopes is presented in Fig. 6. The single natural bismuth isotope is not detected at mass 209 amu ($^{209}Bi^{+}$) due probably to a very low ionization rate. The natural isotopic ratio of lead is

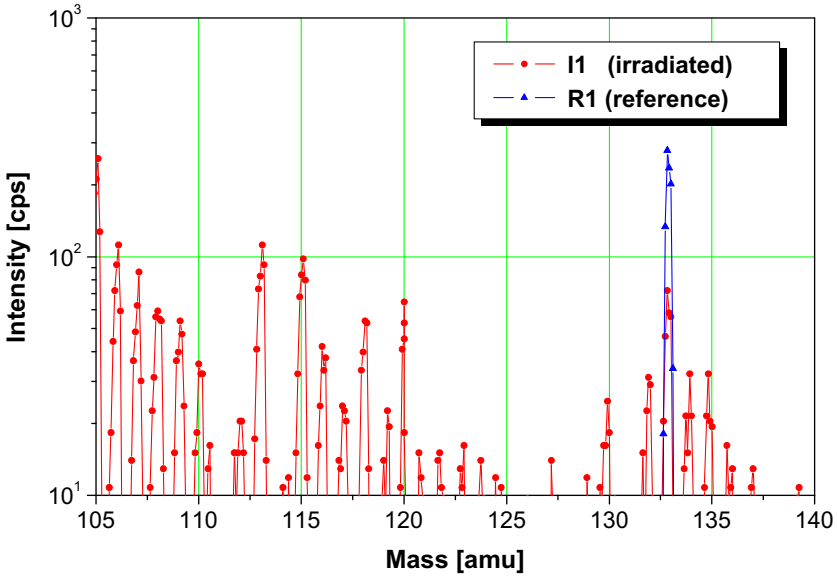

Fig. 5. Mass scans comparison between both specimens in range 105–140 amu.

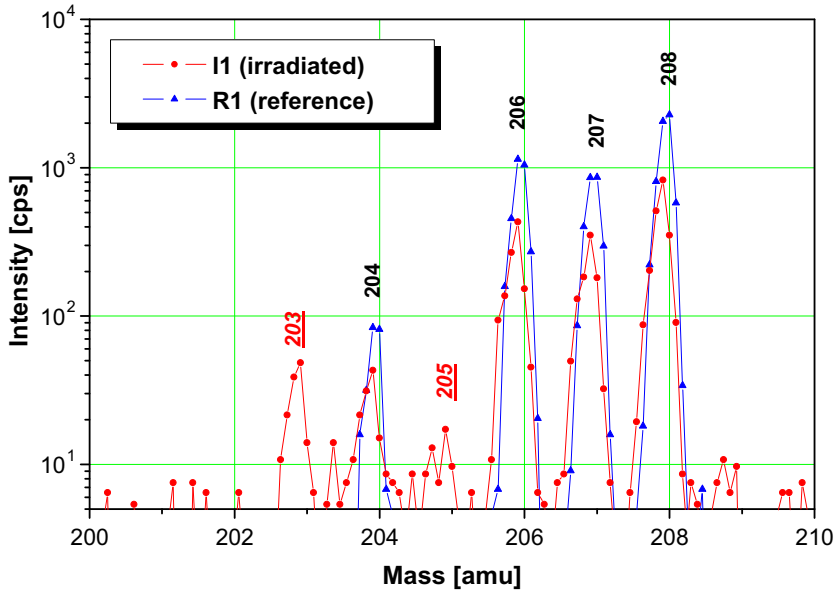

Fig. 6. Mass scans comparison between both specimens in range 200–210 amu.

Table 2
Pb isotopic ratio measured in both specimens on the MS

Sample	Isotope (amu)	Natural isotopic ratio (%)	Measured isotopic ratio (%)	Deviation (%)
R1	$^{204}Pb^{+}$	1.4	1.3	7
	^{206}Pb	24.1	26.3	9
	$^{207}Pb^{+}$	22.1	19.9	10
	$^{208}Pb^{+}$	52.4	52.5	0
I1	$^{204}Pb^{+}$	1.4	2.6	86
	^{206}Pb	24.1	26.2	9
	$^{207}Pb^{+}$	22.1	21.3	4
	$^{208}Pb^{+}$	52.4	49.9	5

Table 3
Pb isotopic ratio measured in specimens I1 on high resolution MS

Sample	Isotope (amu)	Natural isotopic ratio (%)	Measured isotopic ratio (%)	Deviation (%)
I1	$^{204}Pb^{+}$	1.4	0.9	36
	^{206}Pb	24.1	26.4	10
	$^{207}Pb^{+}$	22.1	21.6	2
	$^{208}Pb^{+}$	52.4	51.1	2

correctly obtained by SIMS on the reference specimen R1 as it can be seen in Table 2. Slightly lower peak intensities are observed in the irradiated specimen I1 for the isotopes ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb (Fig. 6). This is probably due to spallation and transmutation processes. This analysis is confirmed by the measurement of peaks at mass 203 and 205 corresponding to isotopes ^{203}Ti and $^{205}Pb/^{205}Ti$. The isotopic ratio calculated from the peak intensity in the irradiated specimen is basically the natural one which is no surprise as the spallation and transmutation processes should not change significantly this macro parameter (see Table 3).

Above of mass 208 amu up to 300 amu no isotopes are clearly detected.

Table 4
Table of the used mass setup during the line-scans

Mass (amu)	Isotope
191	$^{191}Ir^{+}$
192	$^{192}Pt^{+}$
193	$^{193}Pt/Ir^{+}$
194	$^{194}Pt^{+}$
195	$^{195}Pt^{+}$
197	$^{197}Au^{+}$
203	$^{203}Tl^{+}$
204	$^{204}Pb^{+}$
205	$^{205}Ti/Pb^{+}$
206	$^{206}Pb^{+}$
207	$^{207}Pb^{+}$
208	$^{208}Pb^{+}$

A higher resolution mass scan realized with different acquisition parameters on the irradiated specimen I1 confirms the isotopic ration obtained in the first analysis (Table 2).

3.2. Line-scan results of both samples

In order to determine possible variation of some relevant isotope concentration distribution across the pellet diameter, line-scans have been realized on both specimens.

The list of the mass acquired during the line-scans and the corresponding isotopes are given in Table 4. The line-scans in the reference specimen R1 were carried out only with the natural Pb isotopes.

The isotope distributions across the rod cross-section are basically constant before and after irradiation as it can be seen in Figs. 7 and 8. The slight signal variation along the scan is produced by a small change of the work function σ [2]. This change is related to the presence of smeared material (from the polishing process) or/and small local composition modification caused by spallation and activation processes.

4. Discussion

The specimen I1 has been analyzed after a cooling time of about two years. Therefore most of the short lived spallation and activation products have decayed into stables or long lived ones.

There is not many published data on the long lived spallation and activation product production in Pb–Bi under mixed proton and neutron irradiation. Therefore it is difficult to compare precisely the experimental data generated in this study with representative data or calculations.

Stankovsky et al. [3] have published experimental and calculated values for the production of short lived isotopes in a thick lead target after 1 GeV proton irradiation. The data set focus only on short lived isotopes therefore it is very difficult to compare them to our data even taking account the decay chains. Other set of data have been published by Donadille et al. [4,6] and Leray et al. [5] using improved version of intra-nuclear cascade and evaporation fission models. These calculations show a good agreement with the data generated within the HINDAS high Energy program for irradiation with slightly higher energy protons than in the SINQ case (1 GeV).

In the Stankovsky paper, a calculation of the mass number distribution of spallation products in Pb irradiated by 0.8 GeV protons is presented (near the 600 MeV proton beam in SINQ). The shape of the distribution is in relatively good agreement with the results of this study for the mass range between 50 and 140 considering the long cooling time of our specimen. However we do not observe the high production rate of elements predicted in the mass range 130–200 amu. In this mass range, the calculations presented in the Donadville and Leray papers show similar high production rates. This a relevant observation as some rare earth elements in this mass range (145–155 amu) have long lived alpha-emitter that rise question on the overall toxicity of spallation targets.

We also observe the production of some isotopes in the lower mass range (10–50 amu) which is not predicted by the simulation by Stankosvsky. However, the newer calculations by Donadille [6] and Leray [5] show a clear production of light elements through a high energy fission channel. Due to the fact that a raw of light elements are present in the reference material as impurities, we cannot sort out the real source of the light elements observed by SIMS between the direct production from Pb irradiation or the production of spallation and activation products in the alloying elements.

Finally, the line-scans realized on the irradiated specimen show a homogeneous distribution of the spallation and activation products in the rod after irradiation.

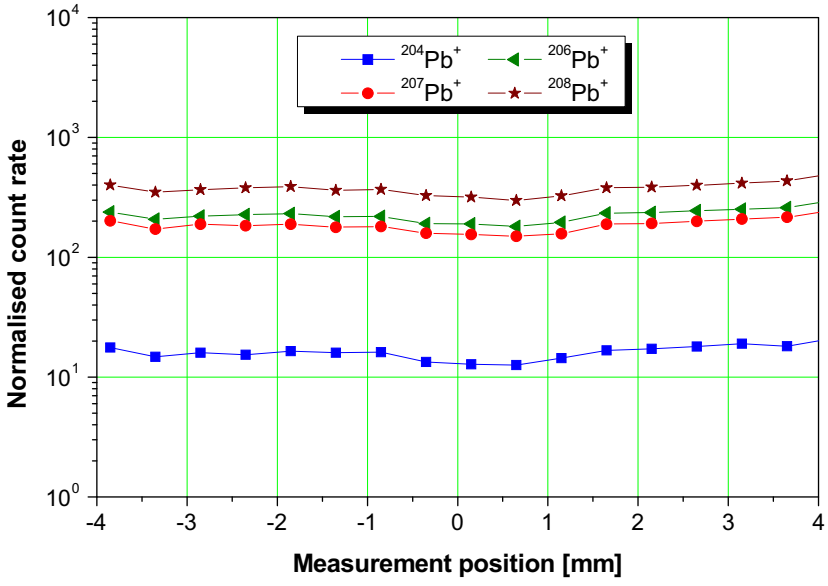

Fig. 7. Relative concentration distributions of some isotopes along a diameter of specimen R1.

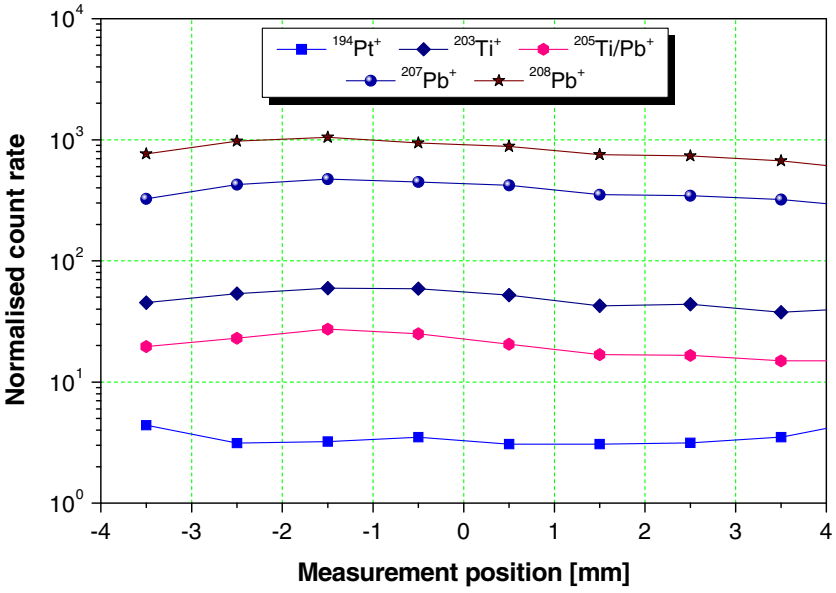

Fig. 8. Relative concentration distributions of some isotopes along a diameter of specimen I1.

5. Conclusion

The secondary ion mass spectrometry measurements realized on a cross-section of a lead rod irradiated in a proton/neutron mixed spectrum show clearly the production of spallation and activation products in the Pb–Bi. The line-scans realized across the diameter of the specimen show the good homogeneity of the materials and prove that the local Mass scans are representative of isotopic content of the material.

Mass scans realized at different position in the material give a overall information on the long lived spallation and activation product mass distribution in lead after irradiation in mixed spectrum.

A partial quantification of the SIMS data could be realized by correlating them with micro gamma spectroscopy analyses that are unhappily not realizable in our laboratory.

References

[1] Y. Dai, X. Jia, R. Thermer, D. Hamaguchi, K. Geissmann, E. Lehmann, H.P. Linder, M. James, F. Gröschel, W. Wagner, G.S. Bauer, J. Nucl. Mater. 343 (2005) 33.
[2] Benninghoven, F.G. Rüdenauer, H.W. Werner, Secondary Ion Mass Spectrometry, vol. 86, 1987.
[3] Alexey Stankovsky, Masaki Saito, Vladimir Artiyuk, Antolii Shmelev, Yuri Korovin, J. Nucl. Sci. Technol. 38 (7) (2001) 503.
[4] L. Donadille, A. Boubard, J.C. David, S. Leray, C. Volant, J. Nucl. Sci. Technol. (Suppl. 2) (2002) 194. August.
[5] S. Leray, A. Boubard, J.C. David, L. Donaddille, C. Villagrasa, C. Volant, in: Proceeding of the International Workshop on P&T and ADS Development 2003, SCK/CEN, October 6–8 2003, <http://www3.sckcen.be/sckcen_en/activities/conf/conferences/20031006/cd/>.
[6] L. Donadille, A. Boudard, J.C. David, S. Leray, C. Volant, International Meeting on Nuclear Applications of Accelerator Technology: Accelerator Application in a Nuclear Renaissance, 2003, p. 1033