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A low-energy set-up for gamma-ray spectrometry of NORM tailored to the needs of a secondary smelting facility

G. Lutter [a], I. Vandael Schreurs [b], T. Croymans [b], W. Schroeyers [b], S. Schreurs [b], M. Hult [a], G Marissens [a], H. Stroh [a], F. Tzika [a]
a) European Commission, Joint Research Centre (JRC-Geel), Retieseweg 111, B-2440 Geel, Belgium
b) Hasselt University, NuTeC, CMK, Nuclear Technology – Faculty of Engineering Technology, Agoralaan Building H, B-3590 Diepenbeek, Belgium

ABSTRACT

A measurements station dedicated for robust quantitative radiological characterisation of naturally occurring radionuclides in a metallurgical company and based on gamma-ray spectrometry was developed. The station is intended for performing quality control of final non-ferrous metal products and for radiological checks of incoming materials. A low-background point-contact HPGe-detector was used and the signal was split in two branches to enable collecting simultaneously spectra with high amplification (for gamma-ray energies below 250 keV) and low amplification.

Keywords: ^{210}Pb; ^{210}Po; metallurgy; industry; gamma-ray spectrometry; naturally occurring radionuclides

Highlights:

- A gamma-ray spectrometer was installed in a secondary smelting facility.
- The set-up and software is optimised for reliable and cost-effective monitoring.
- Incoming materials and final products can be monitored.
- It is focused on simultaneous measurement of ^{210}Pb and ^{210}Po.
- Decision limits and detection limits are given for ^{210}Pb and ^{210}Po.

1. Introduction

In the context of striving for a sustainable society, industrial residue is increasingly used as input-material for certain industries. Many metals can for example be extracted and recycled in this way. In the frame of the European project "MetroNORM" (Metrology for processing materials with high natural radioactivity) several European NMIs (National Metrological Institutes) have worked together to develop new radiological methods adopted for measuring NORM (Naturally Occurring Radioactive Materials) and to produce reference materials suitable for testing these new methods. MetroNORM was also a direct response to the new EURATOM Basic Safety Standards (EU-BSS) that were published in 2014 and should be transposed to national law before February 2018 (The Council of the European Union, 2013). The EU-BSS regulates NORM and have listed 16 important industries for this in annex VI.

One work package (No. 5) of MetroNORM deals with *on-site* measurements at industries. Five companies in different industrial branches were selected and specially designed measurement stations were developed, installed and tested there. This paper deals with a gamma-ray spectrometry measurement station developed for a secondary smelter facility for non-ferrous metal production. It sorts under the heading tin/lead/copper smelting in annex VI of the EU-BSS. The factory handles a broad range of primary and secondary raw materials coming from industries also listed in annex VI of the EU-BSS.

The incoming products are traded at global scale and according to the company, non-compliant deliveries are increasingly frequently observed, which highlights the importance of rapid monitoring. The activity concentrations of the natural radionuclides in the feedstock are heterogeneous, due to origin and geochemical properties of the primary raw materials and the pre-processing of the secondary raw materials. In addition, it has been observed that activity concentrations in the output products from the metallurgical industries can vary greatly

depending on the input material, the production process and the chemical and physical properties of the radionuclides (Croymans, 2016).

The main focus of this paper is measurement of the naturally occurring radionuclides ^{210}Pb and its alpha-emitting grand-daughter ^{210}Po in the lead containing metallic output products. The equilibrium between the ^{210}Pb and ^{210}Po cannot be assumed and possible contamination of ^{210}Pb and/or ^{210}Po cannot be excluded. Therefore, the measurement of both radionuclides is required.

The presented set-up and the associated software were designed in such a way as to enable adequate and relatively rapid and cost-effective monitoring of both incoming material and final products. By enabling the company to perform these measurements *on-site* they will obtain information on possible contamination and possible non-compliant deliveries much faster than at present. Like most non-nuclear industries, the company has only limited equipment and skills for quantitative radiological characterisation. Therefore an important aspect of the measurement station was its autonomy and simple and robust operation. For this reason no alpha-particle spectrometry was used for the determination of ^{210}Po. Since the gamma-ray emissions of ^{210}Po are very weak an important aspect of this work was to study what detection limits were possible for ^{210}Po using gamma-ray spectrometry, which called for some insight into low-level techniques. In addition to ^{210}Pb and ^{210}Po, other primordial radionuclides that can be detected using gamma-ray spectrometry are also monitored.

The metallic output products are not end-products for consumers. Instead they are used by other metal handling industries. The ^{210}Pb and ^{210}Po exemption limits, following the EU-BSS, are 1 Bq/g when secular equilibrium in the whole ^{238}U decay chain is present. In the case of

absence of equilibrium, higher values can be applied. These higher values are not specified in the EU-BSS. The technical guide Radiation Protection (RP) 122 part II (European Commission, 2002) specifies the exemption and clearance levels even when the secular equilibrium is absent, namely 5 Bq/g for ^{210}Pb and ^{210}Po. Although these limits of radioactivity are relatively high (from a low-level measurement technique perspective), it was important to design the measurement process such that rapid monitoring of lower concentrations was possible to obtain a time-series of the activity. Making correlations between activities in input-materials and output would potentially enable a better steering of processes and improving quality of products. In fact radio-impurities can be used as tracers for certain process also in industry.

2. Materials and Methods

2.1 Gamma-ray spectrometry station

The measurement station was based on low-background point-contact HPGe-detector with a thin top deadlayer; a so-called BEGe-detector from Canberra, with a crystal radius of 30.5 mm. It was installed in a low-background lead/copper shield inside the chemistry laboratory of the company. The detector was equipped with a hybride-cryostat (Cryo-cycle II) filled with liquid nitrogen that is condensed as it boils off. This enables operation times of at least a year without having to refill liquid nitrogen. Advantages of this compared to electrical cooling without LN_2 are that the cooling is not interrupted in case of a power cut and that the Ge-crystal has a lower temperature which gives a slightly better energy-resolution. For this set-up the resolution (FWHM) was 0.50 keV at 46.5 keV, 1.30 keV at 803 keV and 1.60 keV at 1332 keV. The shield consisted of 1 mm electrolytic copper on the inside and then 5 cm low-background lead (2 Bq/kg of ^{210}Pb) and outmost, 5 cm of standard lead with ^{210}Pb activity 50 Bq/kg.

For characterising the final product it was important to realise simultaneous determination of ^{210}Pb (half-life 22.23 years) using the 46.54 keV gamma-ray with an emission probability of 4.252(40)% and its grand-daughter ^{210}Po (half-life 138.4 days) using the very weak 803.05 keV transition with an emission probability of only 0.00123(4)%. The 803.05 keV gamma line is the only gamma-ray following the decay of ^{210}Po. For completeness it should be mentioned that there are also Pb X-rays following the ^{210}Po decay but they cannot be used for quantification due to the low emission rate and for interference with fluorescence X-rays from the sample. The daughter of ^{210}Pb is ^{210}Bi (half-life 5.01 days), which decays to the ground state of ^{210}Po. A major "problem" with ^{210}Bi in gamma-ray spectrometry is that it generates a bremsstrahlung background with an end-point energy of 1161 keV, which contributes to deteriorating the detection limits for many gamma-rays.

The HPGe-detector got high voltage and the pre-amplifier got power from a single box digital unit (Lynx, Canberra). The output signal of the detector was, however, split in two branches and fed to both the first Lynx and a second one to enable generation of two spectra simultaneously as recommended for analysis of gamma-rays of both high and low energy (Hult, 2007; Hult et al., 2012). The spectrum with high amplification (0.1 keV/channel) reached up to 850 keV so that a source of ^{137}Cs could be used for calibration and the 803 keV peak could be seen. The spectrum with low amplification (0.33 keV/channel) reached 2700 keV so that the 2614 keV peak from ^{208}Tl could be detected.

2.2 Samples

The system was developed for two main types of samples: non-ferrous metal cylinders (diameter: 30 mm; height: 17 mm) and 100 mL plastic containers filled to their full height of

60 mm with non-ferrous slag. The mass of the cylinders was around 150 g and depends on the relative amount of the non-ferrous metals present and the small differences in size between the collected samples. Some samples with elevated activities were supplied for the sake of enabling quantification of ^{210}Pb and ^{210}Po using gamma-ray spectrometry. The preparation of the slag (input material) involved crushing and sieving. The radon-daughters ^{214}Bi and ^{214}Pb were used for quantifying ^{226}Ra. To achieve this, it was asked to re-measure the sample after at least 2 weeks standing time so that secular equilibrium could be (almost) established between ^{222}Rn and its daughters. In the analysis following immediately after sample preparation a "rough" value (value with higher uncertainty) for ^{226}Ra was produced based on analysis based on the 186 keV line. The interfering contribution from ^{235}U to this line was subtracted after determining the ^{238}U activity and assuming a natural isotopic abundance of uranium.

2.3 Software for data acquisition and analysis

For *on-site* measurements a software using the Canberra Genie-2000 libraries was developed in MS Visual Basic. The software performs data acquisition, energy calibration, automatic data analysis and activity calculations with few inputs from the operator (e.g. sample name, mass and composition). The main objective was to make it very user-friendly which lead to the necessity of limiting its applicability to the two types of samples mentioned above and to the gamma-ray emitting radionuclides in the ^{238}U and ^{232}Th decay chains together with ^{40}K and ^{137}Cs. To simplify the activity calculations, only the gamma-rays with an emission probability higher than 1% and without any interference with other gamma-lines common in these samples were taken into account.

3. Results

All detection limits and decision thresholds in this article are calculated using the standard ISO 11929:2010 (ISO, 2010) with the confidence level 90%.

Figure 1 shows the spectrum collected using Ge-T6 on-site of a non-ferrous metal sample with 47% (by mass) of Pb. Data was collected for 20 hours and it is possible to see the peaks of both ^{210}Pb and ^{210}Po. In this sample, there is equilibrium between the two radionuclides and the activity is 6.5 kBq, which converts to a massic activity of 43 Bq/g. Furthermore, it can be observed that none of the other naturally occurring radionuclides are present in the spectrum.

Figure 2 shows a zoom of the spectrum in Fig. 1 at 46.5 keV. In the same figure the spectrum that was collected simultaneously using the second digital box with high amplification (0.1 keV/channel is displayed. It is evident that the peak definition is much better with more channels given that there are enough counts in the peak. The low amplification spectrum has merely 3 channels per peak which will not result in a visibly Gaussian shape. The background spectrum of Ge-T6 is also displayed in Figure 2. For reference, the background spectrum of a low-background detector ("Ge-T2") of similar volume but with a coaxial shape is displayed. Ge-T2 is located in the radionuclide metrology laboratory of JRC-Geel, which is kept very clean and with a controlled atmosphere. It is also shielded by 10 cm lead and 2mm copper but the innermost lead has a ^{210}Pb activity of 2 Bq/kg.

Figure 3 shows again a zoom of the spectrum in Fig.1 but this time at 803 keV. The spectrum with high amplification is not shown as the peak definition in this case is not so good due to the poor counting statistics in each channel. In this case the low amplification spectrum gives at least 5 channels for the peak which is considered acceptable. There is a peak at 803.5 keV in

the background spectra. It has about the same area in the two different detectors. This peak is from inelastic scattering of neutrons in ^{206}Pb. The energy difference between the two peaks is too small to allow for a deconvolution of the peaks unless they are of about similar size and known with good counting statistics (which is rarely the case). It is best to subtract the count rate from this background peak. The uncertainty of the count-rate of the background peak need to be composed of both the counting statistical uncertainty from a long measurement (2 weeks) and the standard deviation of the count-rate after measuring this background peak regularly over a long period of time. The latter is necessary as the peak count rate varies with time as it is linked to the cosmic rays. This highlights again the need for keeping a timeline of the count-rates of all background peaks. An analysis of the sources that contribute to the continuum under the 803 keV peak (and the peak from inelastic scattering) is shown in Table 1. It is based on the measurement of the sample shown in Figure 1. The ^{210}Bi activity is taken to be the same as the ^{210}Pb activity (i.e. 6.5 kBq).

The decision threshold for ^{210}Po in this sample is 9 Bq/g after one day of measurement. A 3.5-days measurement brings the decision threshold down to 4.8 Bq/g. Samples with an activity concentration above the decision threshold but below the detection limit should be measured longer. After 15 days of measurement, the detection limit is 4.8 Bq/g. If no signal has been observed in the meanwhile, the sample fulfilled the regulation (below 5 Bq/g) and can be used.

4. Discussion and conclusion

The present on-site controls are outsourced, samples of incoming materials and lead end-products are sent to an external laboratory for radioactivity measurements. The results of the measurement can take several weeks. The current configuration of this set-up can confirm the

compliancy with regulations within 3 days or maximum 15 days in case of low activity concentration.

Detecting 803 keV from ^{210}Po requires low-level measurements although the activity of ^{210}Po is not very low. Due to the interference with the inelastic scattering of the neutrons in ^{206}Pb, a specific effort on the design of the shield has to be done. One can reduce the detection limits for this type of samples further by removing the peak from inelastic scattering. This can be done, on-site, by adding an extra shield of borated polyethylene or layers of Cd and Paraffin to slow down and capture neutrons. A 5 cm-thick borated polyethylene reduces the continuum under the 803 keV peak by 90%.

The EU-BSS and the technical guide RP122 do not define the calculation method of the decision threshold and detection limit. By using the previous ISO11929-3 from 2000 (ISO, 2000), a decision threshold of 5 Bq/g is reached only after 2.6 days of measurement and the detection limit after less than 11 days. The ISO11929-3 version 2000 is based on the Currie calculation method whereas the most recent version introduces the Guide of the Expression of Uncertainty in Measurement (GUM) in the decision threshold and detection limits calculation. It results to higher values due to the fact of taking into account systematic uncertainties in the calculations (type B uncertainties in the GUM).

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Figure Captions

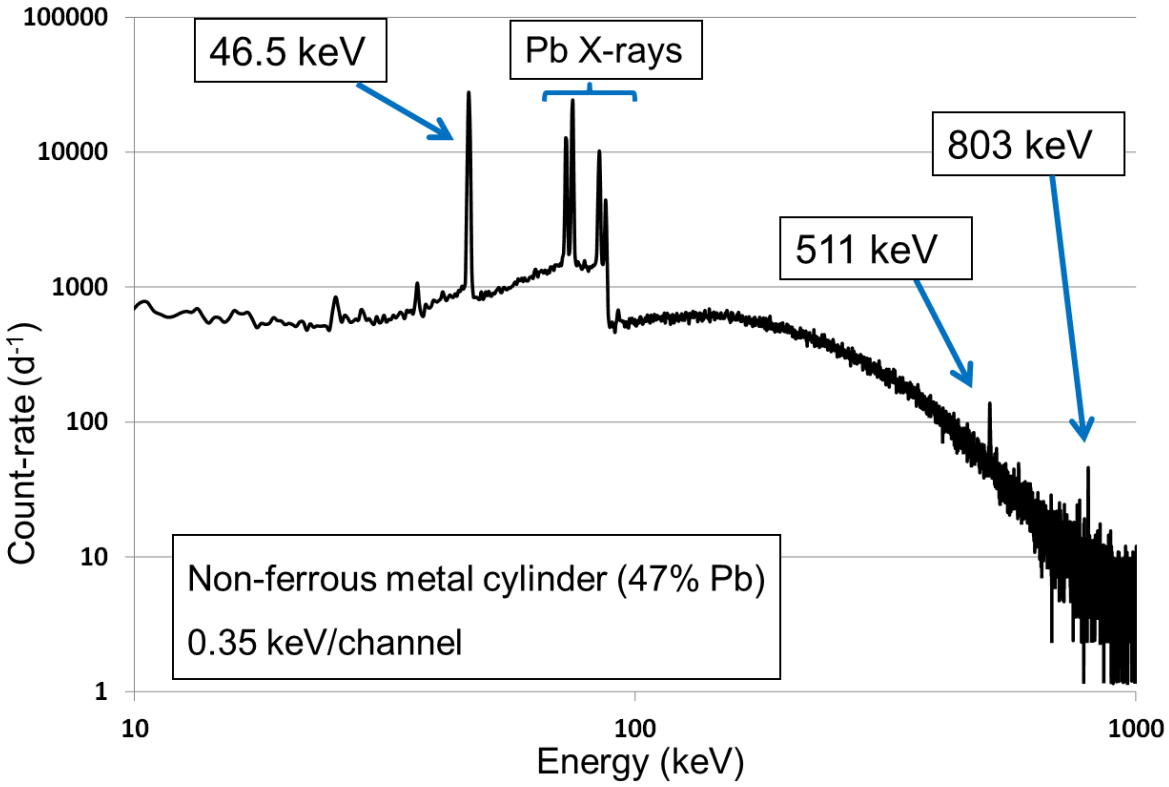
Figure 1. Spectrum from a non-ferrous Pb-containing (47% by mass) sample collected with detector Ge-T6 *on-site* using low amplification. Note that there is log-scale on both axes to better visualize the two peaks at 46.5 keV and 803 keV.

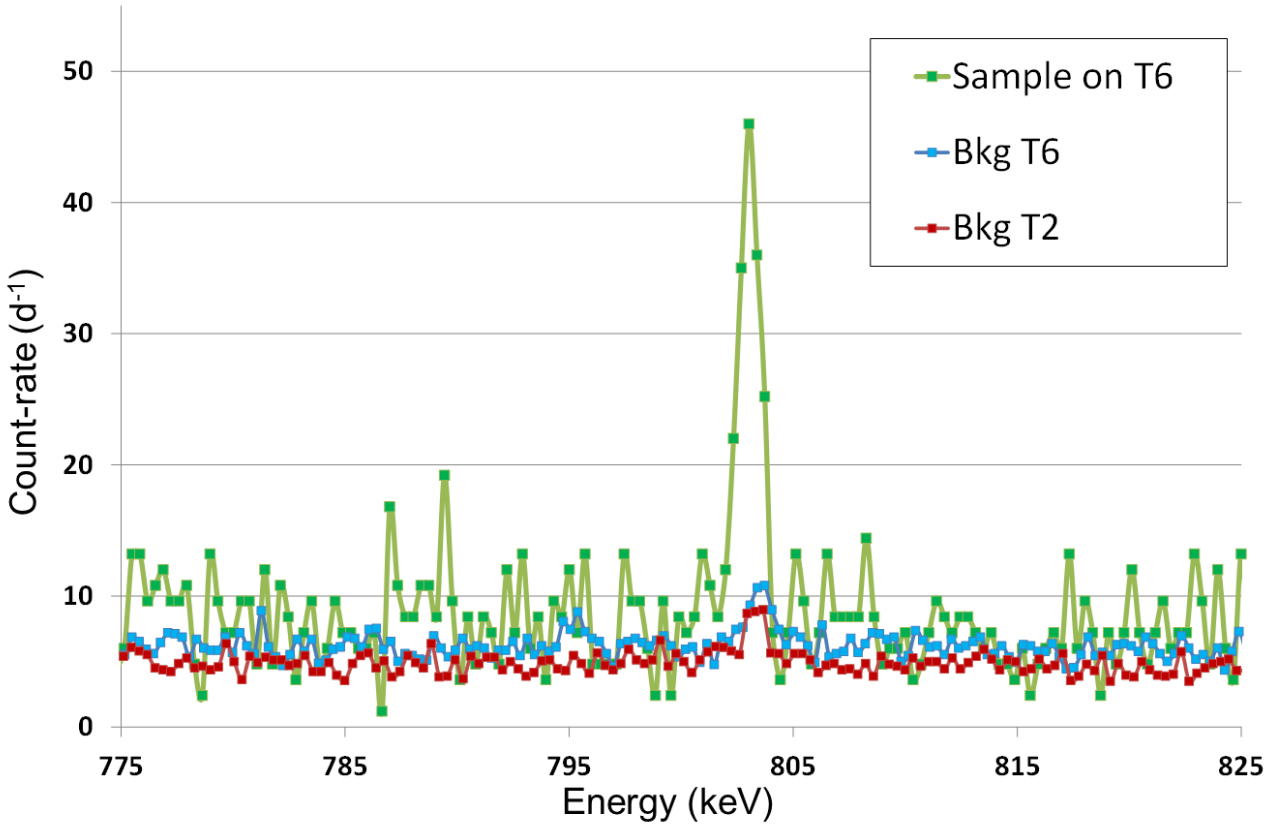
Figure 2. Zoom on the 46.5 keV peak from the spectrum in Figure 1. In addition, the same sample analysed simultaneously with High Amplification (HA) is displayed together with the background of the same detector. For reference, the background of a coaxial low background (T2) is also displayed.

Figure 3. Like Figure 2 but with zoom on the peak at 803 keV.

Table Caption

Table 1 Analysis of continuum and inelastic scattering contribution at a 6.5-keV interval at 803 keV. The sample is a non-ferrous Pb-containing (47% by mass) of 151 g with ^{210}Pb (6.5 kBq) and its daughters in secular equilibrium and ^{40}K (<0.6 Bq). Data is based on measurements carried out in April 2016.


46.5 keV
Pb X-rays
803 keV
511 keV
Non-ferrous metal cylinder (47% Pb)
0.35 keV/channel
Count-rate (d-1)
Energy (keV)
100000
10000
1000
100
10
1
10
100
1000


Sample on T6
Bkg T6
Bkg T2
Count-rate (d-1)
50
40
30
20
10
0
775
785
795
805
815
825
Energy (keV)

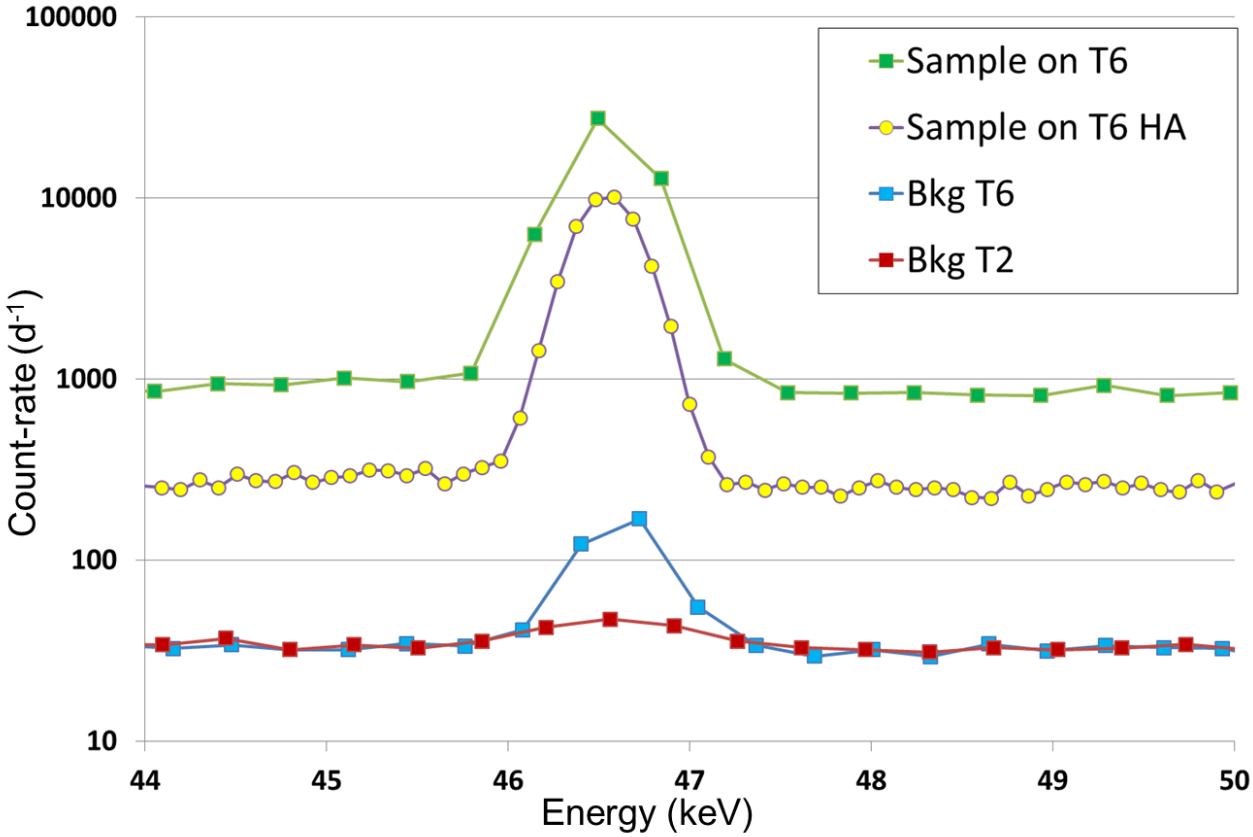

100000
10000
1000
100
10
Count-rate (d-1)
44
45
46
47
48
49
50
Energy (keV)
Sample on T6
Sample on T6 HA
Bkg T6
Bkg T2

Table 1 Analysis of continuum and inelastic scattering contribution at a 6.5-keV interval at 803 keV. The sample is a non-ferrous Pb-containing (47% by mass) of 151 g with ^{210}Pb (6.5 kBq) and its daughters in secular equilibrium and ^{40}K (<0.3 Bq). Data is based on measurements carried out in April 2016.

	Relative contribution of count-rate at 803 keV (except for contribution from ^{210}Po) normalized to the total count rate of column 2.				
Background source	**Installed at metallurgical company**	**Extra shield of 5 cm borated polyethylene**	**Installed underground at a depth of 10 m w.e.**	**Installed underground at a depth of 500 m w.e.**	**A 20% coaxial HPGe-detector in a similar shield**
Bremsstrahlung from ^{210}Bi	9%	12%	37%	89%	5%
Compton scattering from ^{40}K	1%	1%	2%	6%	0%
Inelastic scattering of ^{206}Pb	27%	4%	10%	2%	15%
Bremsstrahlung from muons	62%	82%	49%	0%	80%
Other sources (e.g. Rn and, impurities)	1%	1%	2%	3%	0%
Counts per day under the 803 keV peak	80	60	20	10	95
Decision threshold for ^{210}Po after a 1-day measurements	9.0 Bq/g	7.5 Bq/g	6.3 Bq/g	6.0 Bq/g	12.7 Bq/g
Measurement time needed to reach a decision threshold of 5 Bq/g	3.3 d	2.3 d	1.6 d	1.5 d	6.4 d