



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



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### ABSTRACT

A measurement station dedicated for 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.

### 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 et al., submitted for publication).

The main focus of this paper is the measurement of the naturally occurring radionuclides <sup>210</sup>Pb and its alpha-emitting grand-daughter <sup>210</sup>Po in the lead containing metallic output products. The equilibrium between the <sup>210</sup>Pb and <sup>210</sup>Po cannot be assumed and possible contamination of <sup>210</sup>Pb and/or <sup>210</sup>Po cannot be excluded. Therefore, the measurement of both radionuclides is required. Note that this paper does not constitute a validation or qualification of the measurement on-site but serve as proof of concept.

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

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measurement station was its autonomy and simple and robust operation. For this reason no alpha-particle spectrometry was used for the determination of  $^{210}\text{Po}$ . Since the gamma-ray emission of  $^{210}\text{Po}$  is very weak, an important aspect of this work was to study what detection limits were possible for  $^{210}\text{Po}$  using gamma-ray spectrometry, which called for some insight into low-level techniques. In addition to  $^{210}\text{Pb}$  and  $^{210}\text{Po}$ , 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  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  exemption limits, following the EU-BSS, are 1 Bq/g when secular equilibrium in the whole  $^{238}\text{U}$  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  $^{210}\text{Pb}$  and  $^{210}\text{Po}$ . 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 hybrid cryostat (Canberra 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  $\text{LN}_2$  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  $^{210}\text{Pb}$ ) and outmost, 5 cm of standard lead with  $^{210}\text{Pb}$  activity 50 Bq/kg.

For characterising the final product it was important to realise simultaneous determination of  $^{210}\text{Pb}$  (half-life 22.23(12) years) using the 46.54 keV gamma-ray with an emission probability of 4.252(40)% and its grand-daughter  $^{210}\text{Po}$  (half-life 138.38(17) 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  $^{210}\text{Po}$ . For completeness it should be mentioned that there are also Pb X-rays following the  $^{210}\text{Po}$  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  $^{210}\text{Pb}$  is  $^{210}\text{Bi}$  (half-life 5.01 days), which decays to the ground state of  $^{210}\text{Po}$ . A major "problem" with  $^{210}\text{Bi}$  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 (Canberra Lynx). 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  $^{137}\text{Cs}$  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  $^{208}\text{Tl}$  could be detected.

### 2.2. Samples

The system was developed for two main types of samples: non-ferrous metal cylinders (diameter: 34 mm; height: 18 mm) and 100 mL plastic containers filled to their full height of 60 mm with non-ferrous slag. The cylinders are routinely collected from the melt following the company's strict quality control procedures for chemical analysis and are representatives of a batch. Their mass is 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. For this study, samples with elevated activities were supplied for the sake of enabling quantification  $^{210}\text{Po}$  using gamma-ray spectrometry. The preparation of the slag (input material) involved crushing and sieving. The radon-daughters  $^{214}\text{Bi}$  and  $^{214}\text{Pb}$  were used for quantifying  $^{226}\text{Ra}$ . 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  $^{222}\text{Rn}$  and its daughters. In the analysis following immediately after sample preparation a "rough" value (value with higher uncertainty) for  $^{226}\text{Ra}$  was produced based on analysis based on the 186 keV line. The interfering contribution from  $^{235}\text{U}$  to this line was subtracted after determining the  $^{238}\text{U}$  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  $^{238}\text{U}$  and  $^{232}\text{Th}$  decay chains together with  $^{40}\text{K}$  and  $^{137}\text{Cs}$ . 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. The full energy peak (FEP) efficiencies of the gamma-rays of interests have been calculated by Monte Carlo simulations. A wide range of simulations have been done to take into account the possible matrix and density differences between the samples. The user enters the

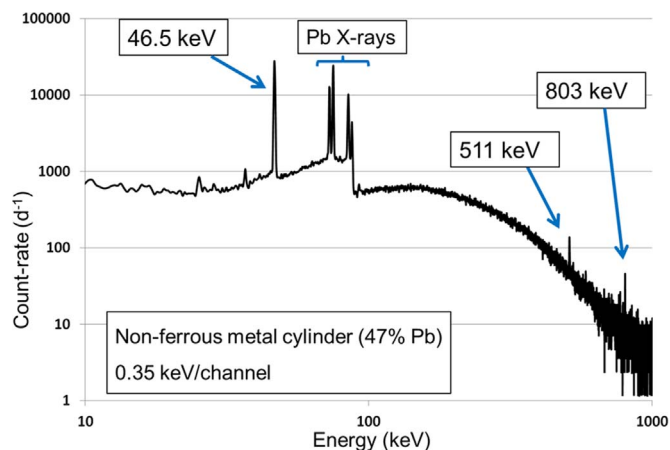


Fig. 1. Spectrum after 20 h of measurement from a non-ferrous Pb-containing (47% by mass) sample of 151 g collected with detector Ge-T6 *on-site* using low amplification. Note that there is log-scale on both axes to better visualize the two peaks at 46.5 keV and 803 keV.

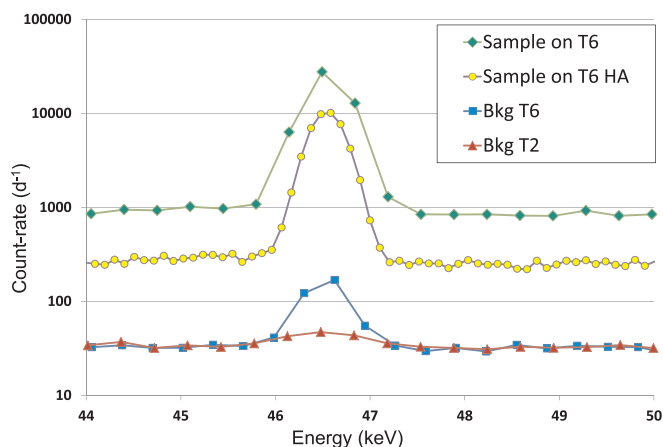


Fig. 2. Zoom on the 46.5 keV peak from the spectrum in Fig. 1. In addition, the same sample analysed simultaneously with High Amplification (HA) is displayed together with the background of the same detector. For reference, the background of a coaxial low background (Ge-T2) is also displayed.

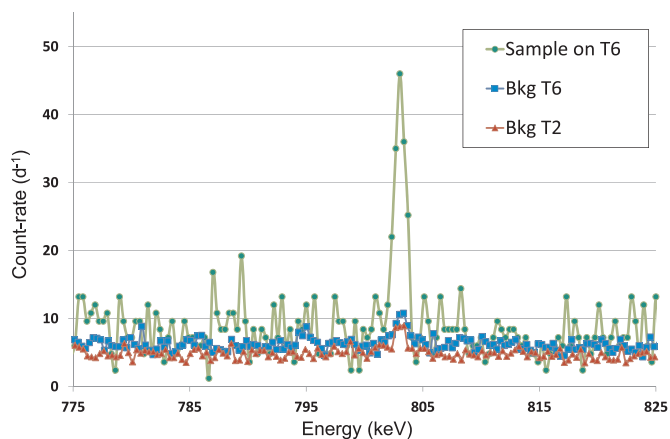


Fig. 3. Like Fig. 2 but with zoom on the peak at 803 keV.

chemical composition based on the standard analyses performed on-site, and then a pre-calculated efficiency is selected by the software.

### 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%.

Fig. 1 shows the spectrum collected using Ge-T6 on-site of a non-ferrous metal sample of 151 g with 47% (by mass) of Pb. Data was collected for 20 h and it is possible to see the peaks of both  $^{210}\text{Pb}$  and  $^{210}\text{Po}$ . In this sample, there is equilibrium between the two radionuclides and the activity is 8 kBq, which converts to a massic activity of 53 Bq/g. Furthermore, it can be observed that none of the other naturally occurring radionuclides are present in the spectrum.

Fig. 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 Fig. 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 2 mm copper. The

innermost lead has a  $^{210}\text{Pb}$  activity of 2 Bq/kg.

Fig. 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 keV in the background spectra. It has about the same area in the two different detectors. The background measurement (with the whole set-up) in the underground laboratory HADES (225 m deep) did not show a peak at 803 keV. Due to the fact that the muon contribution and the induced neutrons could be neglected in the underground laboratory, we conclude that this peak is from inelastic scattering of neutrons in  $^{206}\text{Pb}$ . In addition the underground measurement enabled the determination of the contribution from "other sources". 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 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 and in Fig. 4. It is based on the measurement of the sample shown in Fig. 1. The  $^{210}\text{Bi}$  activity is taken to be the same as the  $^{210}\text{Pb}$  activity (i.e. 8 kBq). The contribution from  $^{40}\text{K}$  and  $^{210}\text{Bi}$  were calculated using Monte Carlo simulations based on the activity determined from the FEP. In order to reduce the count-rate from inelastic neutron scattering on  $^{206}\text{Pb}$  5-cm thick plates of borated polyethylene were placed around the shield (except underneath). It resulted in a 50% reduction of the count rate at 803 keV.

The decision threshold for  $^{210}\text{Po}$  in this sample is 8.5 Bq/g after one day of measurement. A 3-d measurement brings the decision threshold down to 5.0 Bq/g. Samples with an activity concentration above the decision threshold but below the detection limit should be measured longer. After 12 days of measurement, the detection limit is 5.0 Bq/g. The average background count-rate in the 46.5 keV peak is  $(250 \pm 10) \text{ d}^{-1}$ . For a sample similar to the one in Table 1 and Fig. 4, the decision threshold is 0.2 Bq/g after 1 d of measurement.

However, 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 standard ISO11929-3 from 2000 (ISO, 2000), a decision threshold of 5 Bq/g is reached only after 2.3 days of measurement and the detection limit after 9.5 days. The ISO11929-3 version 2000 is based on the Currie calculation method whereas the most recent version requires uncertainty estimates in the calculations. This results in higher values due to systematic uncertainties in the calculations (type B uncertainties in the GUM).

### 4. Discussion and conclusion

At present the company outsources the radiological control samples of incoming materials and lead end-products. Having access to an on-site set-up can drastically speed up feedback of the activity concentrations of important materials in their processes.

Detecting 803 keV from  $^{210}\text{Po}$  requires low-level measurements although the activity of  $^{210}\text{Po}$  may not be very low. Due to the interference with the inelastic scattering of the neutrons in  $^{206}\text{Pb}$ , a specific effort on the design of the shield has to be done. It is not realistic for a company to have a deep underground laboratory. However, a shallow depth laboratory (10 m w.e.) has been realised in many places and our calculations show (Fig. 4) that it could result in a 10-fold reduction of background count-rate at 803 keV. If this is not an option, it is advantageous to work with neutron absorbers as was shown here.

**Table 1**

Analysis of continuum and inelastic scattering contribution at a 3.3-keV interval at 803 keV. The sample is a non-ferrous Pb-containing (47% by mass) cylinder of 151 g with  $^{210}\text{Pb}$  (8 kBq) and its daughters in secular equilibrium.

Background source	Relative contribution of count-rate at 803 keV (except for contribution from $^{210}\text{Po}$ -peak)				
	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 of $^{210}\text{B}$ from sample	9%	12%	37%	90%	5%
Compton scattering of $^{40}\text{K}$ from background	1%	1%	2%	6%	0%
Inelastic scattering of $^{206}\text{Pb}$	27%	4%	11%	2%	14%
Bremsstrahlung from muons	62%	82%	49%	0%	80%
Other sources (e.g. Rn and, impurities)	1%	1%	1%	2%	1%
Counts per day under the 803 keV peak	80	60	20	10	95
Decision threshold for $^{210}\text{Po}$ after a 1-d 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	1.4 d	6.4 d

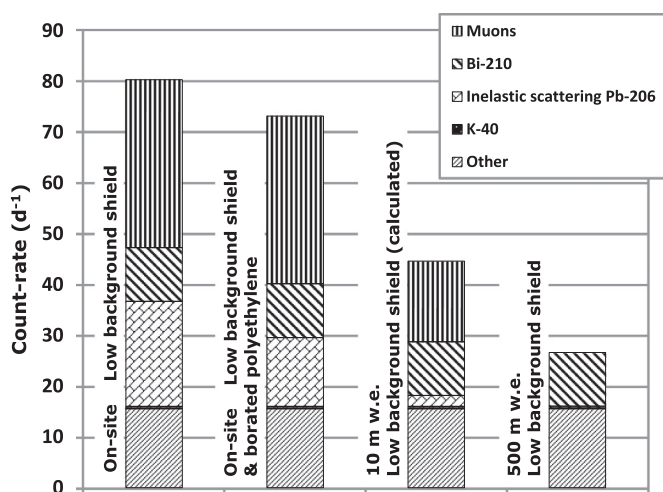


Fig. 4. The count rate at 803 keV from a non-ferrous Pb-containing (47% by mass) cylinder of 151 g with  $^{210}\text{Pb}$  (8 kBq) and its daughters in secular equilibrium, similar to Table 1.

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