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The MEDINA facility for the assay of the chemotoxic inventory of radioactive waste packages

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Abstract A new analytical facility called MEDINA (Multi Element Determination based on Instrumental Neutron Activation) and based on Prompt- and Delayed-Gamma-Neutron-Activation-Analysis (P&DGNAA) using a 14 MeV neutron generator is developed for the determination of non-radioactive elements and substances in 200-l radioactive waste drums. The qualitative performance of MEDINA is studied by measuring (1) the gamma-ray spectra for the empty chamber, (2) for an empty 200-l steel drum in presence or not of ^{60}Co and ^{137}Cs sources and (3) for a 200-l steel drum filled with concrete in order to determine the level of interferences induced by activation products of the facility components and to investigate further optimization steps to improve the measurements sensitivity. The measurement carried out for the empty drum with the radioactive sources show the possibility to characterize radioactive waste packages containing both ^{60}Co and ^{137}Cs with activities ranging between 20 and 80 MBq at least.

Keywords P&DGNAA · Radioactive waste · Chemotoxic inventory · Concrete · MEDINA

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Introduction

In addition to the radioactive components, radioactive waste may contain non-radioactive chemically toxic inorganic and organic substances that can adversely affect human health and the environment [1]. After an adequate decay time the radioactivity of the waste will become non-hazardous but the chemically toxic substances will persist. To comply with the European regulation [2], the disposal of radioactive waste must avoid any pollution of ground water from toxic chemicals, even long after the radioactivity of the waste has reached levels of natural radioactivity [3]. Consequently, the chemotoxic inventory of radioactive waste packages has to be considered in the long term safety assessment of every repository of the EU member states. In Germany, the Federal Office for Radiation Protection (Bundesamt für Strahlenschutz) has defined acceptability limits regarding 94 substances hazardous to water for the disposal of radioactive waste with negligible heat generation in the repository Konrad [4].

In principle, these hazardous substances may be quantified from traceability and quality controls performed during the waste production and conditioning processes. However, poor or no information is available for the so-called historical wastes that need to be characterized retrospectively. As a consequence, a R&D program was initiated in 2006 with the aim to develop a nondestructive analytical technique based on prompt and delayed gamma neutron activation analysis (P&DGNAA) for the identification and quantification of toxic substances in radioactive waste packages. In a first study conducted between 2007 and 2010, it was experimentally demonstrated that P&DGNAA using a 14 MeV neutron generator is suitable to determine the chemical composition of large samples [5–8]. Based on the results of this study the facility

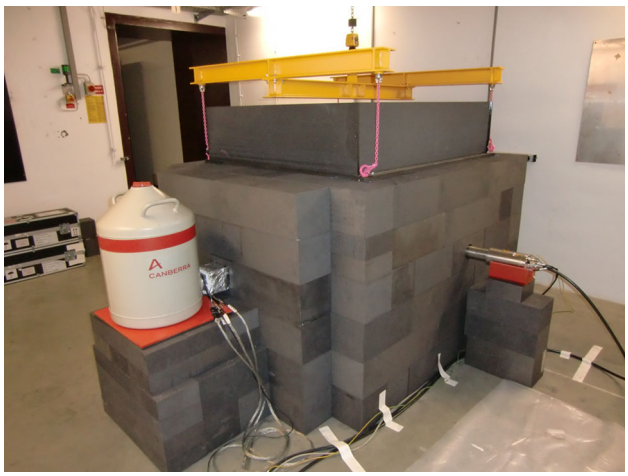

Fig. 1 The facility MEDINA for the assay of 200-l drums with the HPGe-detector in *foreground* and the 14 MeV neutron generator on the *right*. (Color figure online)

MEDINA (Multi Element Detection based on Instrumental Neutron Activation) was designed and built in 2010 for the assay of 200-l drums filled with radioactive waste and its performance was experimentally and numerically investigated [9].

In this work, the facility MEDINA is described. The gamma-ray spectra measured for the empty chamber (active background of the facility), for an empty 200-l steel drum in presence or not of ^{60}Co and ^{137}Cs sources and for a 200-l steel drum filled with a non-radioactive concrete matrix are presented and discussed in view of further optimization steps to improve the measurements sensitivity.

The facility MEDINA

The facility MEDINA designed for the assay of 200-l drums filled with radioactive waste is shown in Fig. 1. The irradiation chamber is made principally of high purity commercial grade graphite (Edelgraphit GmbH) acting as neutron moderator and reflector. The inner dimension of the irradiation chamber is $80 \times 80 \times 120$ cm^3 and the outer dimension is $160 \times 200 \times 155$ cm^3. The wall thickness is 40 cm. The roof construction is a large box made of carbon-fiber reinforced polymers (CFRP) which is completely filled with 30 cm high graphite blocks. The total amount of graphite used to build the chamber is around 6.500 kg. The drum is positioned on a CFRP-turntable fixed to a programmable rotary indexing table (Fibro GmbH) allowing measurements at different rotation angles of the drum. The soil of the chamber around the turn table is covered with 20 cm thick graphite block. A crane is used to lift and remove the roof construction as well as to load a drum into the irradiation chamber. The elemental composition of graphite and CFRP obtained from the PGNAA of samples at the cold neutron beam of the Budapest Research Reactor [10] is given in Table 1.

The drum is irradiated with 14 MeV neutrons produced by a deuterium–tritium (D–T) neutron generator (GENIE 16GT, EADS SODERN). The neutron generator is positioned horizontally in a wall of the irradiation chamber with its tritium-target (Titan doped with 180 GBq Tritium) located at mid-height of the drum. The distance between the tritium-target and the centre of the drum is 55 cm. In this work the neutron generator is operated in pulse mode with an acceleration voltage of 85 kV and a current of 40 μA corresponding to a neutron emission of about 8×10^7 n/s. The length of the neutron pulses corresponding to the 14 MeV neutron irradiation time is set to 50 μs and the repetition period of the neutron pulses to 1 ms.

The detection of the prompt and delayed gamma rays is achieved with a 104 % n-type HPGe-detector (CANBERRA). To avoid thermal neutron activation of the germanium crystal the detector is entirely surrounded by an array of ^{6}LiF plates made of a pressed and dried mixture of ^{6}LiF powder and silicon based water glass [5]. In order to avoid direct contact with graphite the ^{6}LiF-shielding is coated by a thin aluminum foil. The detector is placed in a wall of the irradiation chamber at the mid-height of the drum perpendicular to the neutron generator. The distance between the detector window and the centre of the drum is 105 cm so that the volume of a 200-l drum is fully assayed. The signals of the detector preamplifier (Transistor-Reset) are processed through a fast spectroscopy amplifier with Gated Integrator (CANBERA Model 2022) by a 16 k Multi-Channel-Analyzer (ORTEC Model A^{spec}-927) interfaced to a PC via USB 2.0. The shaping time of the Gated Integrator is set to 0.5 μs providing a good compromise relation between energy resolution and detector dead time. By triggering the Multi-Channel-Analyzer on the start of the neutron pulse via a Digital Delay Generator (Signal Recovery Model 9650A) a delay of 20 μs after the end of the neutron pulses and a counting time of 930 μs between neutron pulses are set. A delay of 20 μs after the pulse is required to avoid fast neutrons induced prompt gamma-rays in the spectrum. The gamma-ray spectra are recorded over a counting time of 1860 s in Zero Dead Time mode with the software GammaVision-32 (ORTEC). The calibration of HPGe-detector in energy and resolution is performed by irradiating a 900 g sodium chloride sample and measuring the prompt gamma-rays of chlorine. The energy resolution ranges from 3.15 keV at 100 to 12.54 keV at 9,000 keV. The analysis of the recorded gamma-ray spectra is carried out with the spectroscopy software Gamma-W (Westmeier GmbH). For the

Table 1 Elemental composition of graphite, carbon-fiber reinforced polymer (CFRP) and concrete determined by PGNAA at the cold neutron beam of the Budapest Research Reactor

Element	Graphite ($n = 2$)	CFRP ($n = 3$)	Concrete ($n = 3$)
Hydrogen	45 ± 21 ppm	2.94 ± 0.05 %	1.40 ± 0.07 %
Boron	1.86 ± 1.39 ppm	1.37 ± 0.15 ppm	94.7 ± 2.2 ppm
Nitrogen	–	4.86 ± 0.06 %	–
Oxygen	–	–	47.3 ± 2.5 %
Sodium	–	–	0.52 ± 0.11 %
Carbon	99.913 ± 0.001 %	92.0 ± 0.3 %	–
Aluminum	405 ± 49 ppm	–	4.9 ± 0.1 %
Silicon	–	–	17.4 ± 0.2 %
Sulfur	115 ± 7 ppm	–	0.67 ± 0.06 %
Chlorine	2.0 ± 1.0 ppm	0.18 ± 0.10 %	200 ± 58 ppm
Potassium	–	–	1.38 ± 0.06 %
Calcium	195 ± 7 ppm	–	23.33 ± 0.58 %
Titan	41 ± 37 ppm	–	0.26 ± 0.01 %
Manganese	–	–	0.068 ± 0.002 %
Vanadium	3.50 ± 3.50 ppm	–	–
Iron	50 ± 14 ppm	–	2.77 ± 0.15 %
Cobalt	–	–	190 ± 101 ppm
Cadmium	–	–	0.48 ± 0.16 ppm
Samarium	73 ± 52 ppb	–	2.22 ± 1.86 ppm
Gadolinium	221 ± 221 ppb	–	4.10 ± 0.17 ppm

The number of samples analyzed is n. The content of oxygen in concrete is estimated assuming that all elements, excepted chlorine, have the maximum oxidation states

identification of the isotopes the prompt gamma ray spectrum catalog of the handbook of prompt gamma activation analysis with neutron beams [11] as well as the IAEA database of prompt gamma rays from slow neutron capture for elemental analysis [12] is used.

Concrete drum

The qualitative performance of MEDINA is studied for a homogeneous concrete drum since most of historical mixed waste is embedded in concrete. The concrete drum is composed of 76 cylindrical concrete bodies (4 layers with 19 bodies each) placed concentrically in a 200-l steel drum. The drum has a filling height of 83 cm and an internal diameter of 56 cm. The wall thickness of the drum is 0.15 cm. The weight of the drum including the top cover is 52.2 kg. According to the drum producer the elemental composition of the steel is 0.12 wt% C, 0.45 wt% P, 0.45 wt% S, 0.60 wt% Mn, and 98.38 wt% Fe. The concrete bodies are fabricated according to a qualified procedure with a special light concrete for the embedding of radioactive waste. The bodies have a height of 20 cm, a diameter of 11 cm and a weight of 2.625 kg resulting in a density of 1.38 g/cm^3. The total amount of concrete in the drum is 199.5 kg and due to the voids the apparent density of the concrete matrix is 1.02 g/cm^3. The elemental composition of the concrete obtained from the PGNAA of samples at the cold neutron beam of the Budapest Research Reactor [10] is given in Table 1.

Measurements

The gamma-ray spectra recorded for the empty chamber, the empty 200-l steel drum and the 200-l drum filled with the concrete matrix are shown together for various energy ranges in Figs. 2, 3 and 4. The identified isotopes are given on the spectra.

The active background spectrum (spectrum displayed in green in Figs. 2, 3 4) is dominated by the prompt gamma-rays of carbon (^{12}C), and hydrogen (^{1}H), as well as by their corresponding single and double escape peaks. Due to the large amount of graphite it is possible to detect the prompt gamma-ray of C-13 at 8,174.04 keV having a very low partial gamma-ray production cross section ($\sigma_{E\gamma} = 1.09 \times 10^{-5}$ b). The major prompt gamma-rays of boron (^{10}B), nitrogen (^{14}N), aluminum (^{27}Al), silicon (^{28}Si), chlorine (^{35}Cl), calcium (^{40}Ca), titan (^{48}Ti), nickel (^{58}Ni), iron (^{54}Fe, ^{56}Fe), samarium (^{149}Sm), and gadolinium (^{155}Gd, ^{157}Gd) are also clearly observed. According to Table 1, the prompt gamma-rays of hydrogen, nitrogen and chlorine are emitted from the components made of CFRP and those of aluminum, calcium and titan from graphite. The prompt gamma-rays of boron are emitted from the CFRP components as well as from graphite. The prompt gamma-rays of

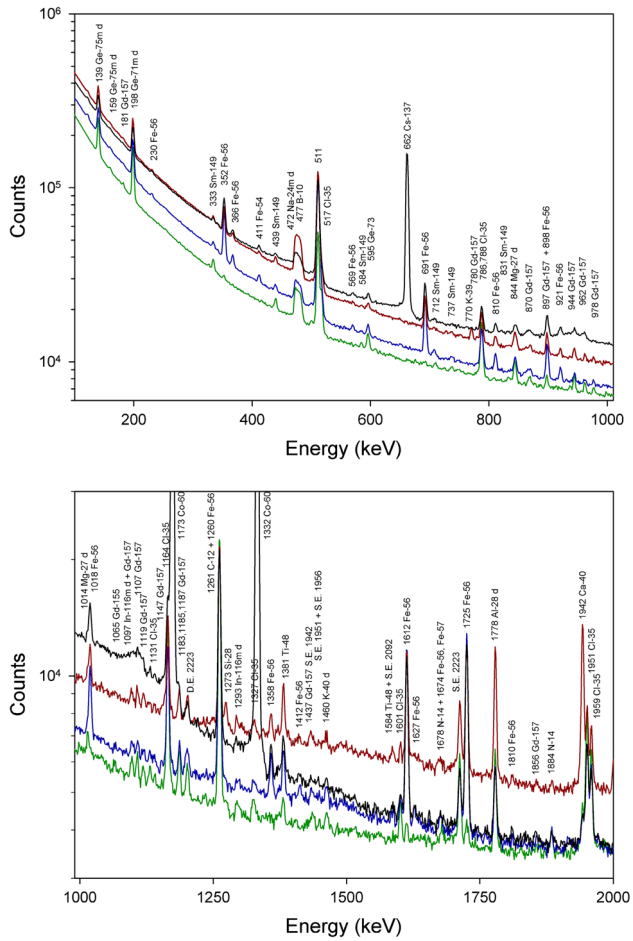

Fig. 2 Gamma-ray spectra in the energy range 100–2,000 keV recorded for the empty cell (*green*), the empty 200-l steel drum (*blue*), the concrete drum (*red*) and the empty 200-l steel drum in presence of ^{137}Cs and ^{60}Co sources (*black*). (Color figure online)

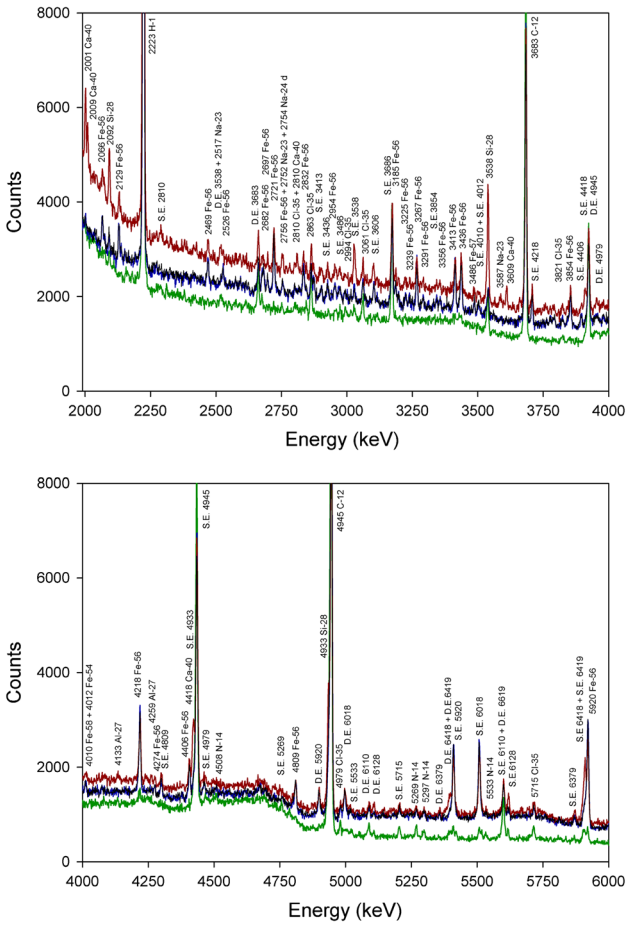

Fig. 3 Gamma-ray spectra in the energy range 2,000–6,000 keV recorded for the empty cell (*green*), the empty 200-l steel drum (*blue*), the concrete drum (*red*) and the empty 200-l steel drum in presence of ^{137}Cs and ^{60}Co sources (*black*). (Color figure online)

titan may be also emitted from the thermal neutron activation of the tritium-target. The prompt gamma-rays of nickel and iron are emitted from the steel housing of the neutron generator. As the neutron generator is embedded in graphite, only the high energy prompt gamma-rays of ^{58}Ni, ^{54}Fe and ^{56}Fe are detected with their associated single and double escape peaks. The prompt gamma-rays of samarium and gadolinium are emitted mainly from the permanent magnet of the step motor in the rotary indexing table. The source for the prompt gamma-rays of silicon is probably the water glass used to fabricate the ^{6}LiF thermal neutron shielding. The prompt gamma-rays of silicon and calcium may be also emitted from the thermal neutron activation of the concrete ground floor. Furthermore the major prompt gamma-ray of ^{73}Ge at 595 keV is observed indicating the leakage of thermal neutrons through the ^{6}LiF shielding. In addition to the prompt gamma-rays, the delayed gamma-rays of the short lived radionuclides, ^{71m}Ge ($T_{½} = 20.4$ ms), ^{75m}Ge ($T_{½} = 47.7$ s), ^{24m}Na ($T_{½} = 20.2$ ms), ^{16}N ($T_{½} = 7.13$ s), ^{28}Al ($T_{½} = 2.24$ m), ^{27}Mg ($T_{½} = 9.46$ m) and ^{116m}In ($T_{½} = 54.3$ m) are observed in the active background spectrum. The isotopes ^{71m}Ge and ^{75m}Ge are induced both through (n,2n)-reactions from the interaction of fast neutrons with the germanium crystal of the HPGe-detector. They decay through the emission of low energy gamma-rays which are fully absorbed in the detector and are responsible in part for the detector dead time. As the prompt gamma-rays of sodium and magnesium are not detected, the isotopes ^{24m}Na and ^{27}Mg are supposed to be produced through (n,α)- and (n,p)-reactions respectively from the interaction of the fast neutrons with the aluminum housing of the HPGe-detector. The isotope ^{28}Al is produced by the interaction of thermal neutrons with the thin aluminum foil coating the ^{6}LiF detector shielding and to some extent with aluminum in graphite. Another possible source of production for ^{28}Al could be the interaction of fast neutrons with silicon in water glass. The isotope ^{16}N is induced through (n,p)-reaction by the interaction of fast neutrons with ^{16}O in graphite or in other material composing the facility. The production of ^{16}N through thermal neutron capture of ^{15}N in the CFRP

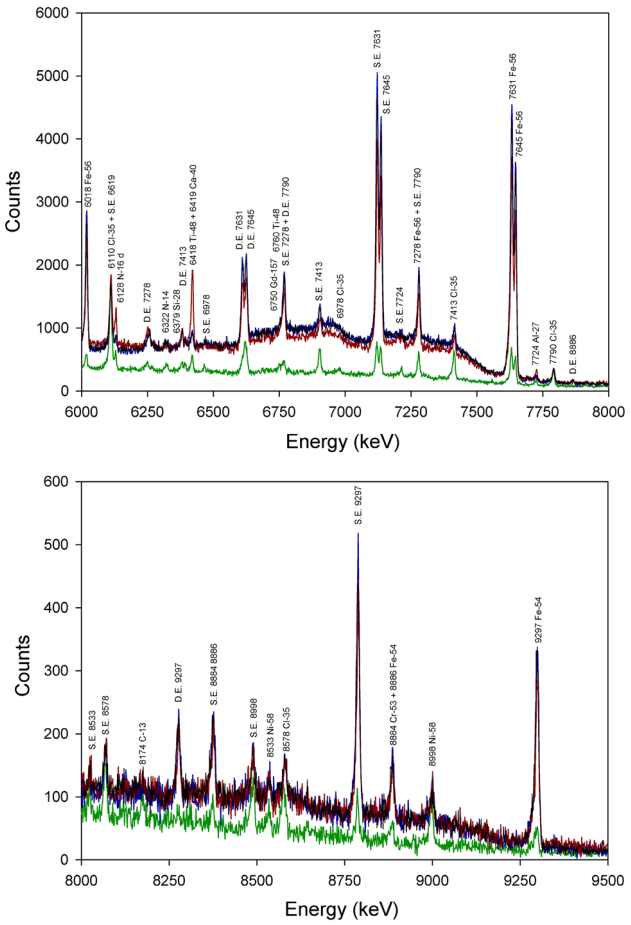

Fig. 4 Gamma-ray spectra in the energy range 6,000–9,500 keV recorded for the empty cell (*green*), the empty 200-l steel drum (*blue*), the concrete drum (*red*) and the empty 200-l steel drum in presence of ^{137}Cs and ^{60}Co sources (*black*). (Color figure online)

components is negligible because of the low partial production cross section of the delayed gamma-ray at 6128.63 keV ($\sigma_{E\gamma} = 5.92 \times 10^{-8}$ b). The isotope ^{116m}In is produced by thermal neutron capture of ^{115}In probably present in the electronics of the neutron generator.

Additionally to the gamma-rays observed in the spectrum of the active background, the gamma-ray spectrum of the 200-l empty steel drum in the energy range 300–9,500 keV (spectrum displayed in blue in Figs. 2, 3, 4) contains the most intense prompt-gamma rays of iron (^{54}Fe, ^{56}Fe, ^{57}Fe). The prompt gamma-rays of the additive elements in steel, such as phosphor, sulfur and manganese are not observed essentially due to their low concentrations. The prompt gamma-ray of ^{48}Ti at 1381.7 keV shows higher counts in comparison to the active background probably due to the presence of titanium oxide as hiding pigment in the yellow paint of the drum.

The gamma-ray spectrum of the concrete drum (spectrum displayed in red in Figs. 2, 3, 4) shows the prompt gamma-rays of hydrogen (^{1}H), boron (^{10}B), sodium (^{23}Na), silicon (^{28}Si), potassium (^{39}K) and calcium (^{40}Ca) as well as the delayed gamma-rays of the short lived radionuclides ^{16}N and ^{28}Al with counts higher than the corresponding gamma-rays observed in the measurement of the empty drum. The isotope ^{16}N is induced through (n,p)-reaction from the interaction of fast neutrons with ^{16}O in concrete. The isotope ^{28}Al is produced by thermal neutron capture of aluminum as well through (n,p)-reaction from the interaction of fast neutrons with silicon. The counts of the prompt gamma-rays of ^{54}Fe, ^{56}Fe and ^{57}Fe induced by thermal neutron activation of the steel drum are lower as in the case of the empty drum due to the gamma-ray absorption of the concrete matrix; the contribution of iron in the concrete matrix being negligible.

The influence of the inventory of gamma-emitting radionuclides on the assay of a radioactive waste drum is investigated through the measurement of the gamma-ray spectrum for the empty drum in presence of ^{60}Co and ^{137}Cs sources (spectrum displayed in black in Figs. 2, 3 4). This approach may be considered as conservative due to the absence of the waste matrix i.e. gamma-ray absorption. ^{60}Co and ^{137}Cs are chosen since they are in most cases the dominating radionuclides in radioactive waste and they are used as key nuclides to determine the activity of difficult-to-measure radionuclides, ^{60}Co being representative for activation and ^{137}Cs for fission products. ^{60}Co and ^{137}Cs point sources with an activity of about 400 kBq each are placed 10 cm behind the HPGe-detector outside of the irradiation chamber indicating a count rate corresponding to 20–80 MBq sources located inside the empty drum. The presence of ^{60}Co and ^{137}Cs increases significantly the background below 1,332 keV affecting the detection of prompt and delayed gamma-rays with low partial gamma-ray production cross sections. Nevertheless the prompt gamma-rays of ^{149}Sm and ^{157}Gd emitted from the permanent magnet of the step motor are still detected in the low energy part of the spectrum. The 1,332.5 keV gamma-ray of ^{60}Co interferes fully with the prompt gamma-ray of ^{35}Cl at 1,327.4 keV. The 1,173.2 keV gamma-ray of ^{60}Co interferes partially with the prompt gamma-ray of ^{35}Cl at 1,164.9 keV and with the prompt gamma-rays of ^{157}Gd at 1,187.9, 1,185.9 and 1,187.1 keV. Above 1,350 keV the gamma-ray spectra recorded for the empty drum with and without the sources are similar so that this region is appropriated for the detection of prompt and delayed gamma-rays in the assay of radioactive waste drums.

Conclusion

A new P&DGNAA facility called MEDINA is developed for the determination of non-radioactive toxic and reactive elements in 200-l radioactive waste drums. It is

demonstrated that MEDINA is a suitable non destructive analytical method to check the chemotoxic inventory of radioactive waste drums containing the major radionuclides ^{60}Co and ^{137}Cs with regards to the acceptability limits defined for their disposal. However, the results show that a shielding of the HPGe-detector against fast neutrons and the high energy prompt gamma-rays emitted by carbon at the vicinity of the detector is required to improve the performance of the facility. Such a shielding could allow the measurement of prompt gamma-rays induced by fast neutrons during the neutron pulses giving so additional information on the radioactive waste composition. Additionally the actual thermal neutron shielding will be replaced by a much more robust one made of pressed and sintered ^{6}LiF plates avoiding so silicon water glass. Moreover some technical modifications concerning the turntable should be carried out to avoid the neutron activation of the permanent magnet of the stepping motor containing the elements samarium and gadolinium.

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