

Using neutron activation analysis (NAA) technique to measure elemental soil and water pollution in the Richards Bay area

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Abstract. Neutron Activation Analysis (NAA) is among the most accurate and reliable analytical techniques that is used for the simultaneous analysis of multiple elements present in a sample. The technique involves exposing samples to a flux of neutrons for a predetermined time and then measuring the emanating characteristic γ -rays from the activated elements using a calibrated γ -ray spectrometer. A successful analysis depends on various factors, such as the neutron energy, neutron flux, and the sample matrix. The aim of this study was to investigate the feasibility of using the technique for routine elemental pollution measurements in soil and water in the Richards Bay area. Richards Bay is an industrialized area and consists of industries that can emit elements such as aluminum, iron, lead, arsenic etc. The calibration of the neutron facility using a mixed metals sample showed the possibility to analyze Al and Fe using 14 MeV neutrons (from the STNG) and that Al can be identified using a neutron flux from the Am-Be source.

1. Introduction

Neutron Activation Analysis (NAA) is considered as one of the most reliable analytical techniques, because of its rapidness and accuracy [1, 2]. The technique has been well developed since it was first introduced in the 1940s, a few years after the discovery of neutrons by James Chadwick in 1932 [3]. The wide range of applications using the NAA technique spans various fields, including industries such as chemical and mining industries. The technique is also employed in archeology and the arts, education, as well as in the environmental pollution applications [4], which is the focus of this study. In this study the feasibility of using the technique to measure elemental pollution in the environment of the Richards Bay area was investigated.

Richards Bay is located in the Northern coast of KwaZulu-Natal, South Africa. The town is one of the industrialized area in the country, with some of the heavy industries found being aluminium smelting, phosphate fertilizer plant, sand dune mining, a kraft-process paper-mill and a coal mine [5]. The industries in the area have typical elements associated with the waste they produce. The phosphate fertilizer industries may release cadmium (Cd), zinc (Zn) and stron-

tium (Sr) into the environment; aluminium smelting activities may release aluminium (Al), lead (Pb), iron (Fe) and manganese (Mn) into the environment, while the Kraft process Paper mill industry may release sulfur (S) and chlorine-based compounds, as well as nitrogen-oxides into the environment [6, 7, 8].

2. Experimental Method

For the study, certified reference materials (CRMs) of soil and water were obtained from Waters ERA, an organization that provides both CRM and proficiency testing (PT) products. Environmental soil and water samples were also collected from three locations around the area of Richards Bay. The water samples were obtained from two water bodies (Mzingazi Dam and a pond situated next to one of the industries) and from a tap drinking water in Esikhawini township using 500 mL polyethylene bottles. Soil samples were collected next to the water bodies and one from the residential homes in Esikhawini, using the same 500 mL polyethylene bottles used to collect water samples. The collected water samples were prepared inside 100 mL cylindrical polyethylene bottles; the soil samples were prepared inside 30 mL cylindrical polyvials. In order to be able to quantify the identified elements using NAA, various standardization methods are used. The comparator method, in which a standard is irradiated along with the sample, was considered because it allows simultaneous analysis of multiple elements. Therefore, the CRMs were also prepared according to the guidelines given in the accompanying certificates. Furthermore, a sample of mixed metals containing 9.8% of Al, 29.1% of Fe, 25% of Zn and 43.4% of nickel (Ni) was prepared inside a glass sample holder for calibrating the facility.

The irradiation was done at the Department of Physics at University of Cape Town (UCT). The neutron sources available are the MP320 sealed tube neutron generator (STNG), which was purchased from Thermo Fisher Scientific [9]; the laboratory in which the STNG was installed was commissioned in 2017 [10]. The Americium-Beryllium (Am-Be) is also available as an additional neutron source. The STNG available is the deuterium-tritium based generator which produces neutrons by accelerating deuterium (^2H) ions towards a tritium (^3H) target. This causes a fusion reaction between ^3H and ^2H , which produces 14 MeV neutrons. As such, the facility is capable of providing a near monoenergetic beam of 14 MeV neutrons with a beam intensity of 10^8 neutrons per second [10]. The STNG is placed inside a compartment where it is shielded with polyethylene blocks and beads.

The Am-Be source was initially stored inside a box with dimensions of $150\text{cm} \times 150\text{cm} \times 150\text{cm}$, in which some of the samples were irradiated. The source has since been moved to the same compartment where the STNG is also installed. Generally, the neutron energies of Am-Be sources range from about 2.5 MeV to 11 MeV, with the average energy being 4 MeV. Also, the neutron flux of a Am-Be source is specified to be 2.2×10^8 n/cm²/s.

Out of the total number of samples prepared only three samples were irradiated using the STNG. These were the mixed metals sample, environmental water sample and a water CRM. This is a result of not observing the γ -rays from the elements interest in the spectrum of the irradiated water CRM. Another reason for not irradiating any further is that the STNG has a limited lifetime of about 1200 hours [9]. The samples were irradiated for 1 hour and were then counted using the HPGe detector. The samples were also irradiated using the Am-Be source while it was still stored inside the box, the remaining samples were irradiated inside the shielding where the STNG is stored. The summary of the irradiation times (t_i), decay times (t_d) and counting times (t_c) is given in tables 1-2.

Table 1. List of samples activated using the STNG.

Sample name	t_i (h)	t_d (s)	t_c (h)
Water-CRM	1	74.13	1
Metallic sample	1	60	1
Art-Road-Water	1	82.94	1

Table 2. List of samples irradiated using the Am-Be source.

Sample Name	t_i (h)	t_d (s)	t_c (s)
Soil-CRM	3.4	135	10800
Art-Road-Soil	3.5	55	7116.442
Metallic sample	5	60	7500.489
ESK-soil	3	180	7220.305
ESK-tapwater	2	180	7213.505
Mz-Soil	2	270	1982.992
Mz-water	9	120	7376.970
Water-CRM	5	60	7500.481

3. Results and discussion

The irradiation of the mixed metals sample, using the STNG, showed a significant response from Fe and Al. Fe was identified by identifying γ -rays from ^{56}Mn , a radioactive product resulting from the $^{56}\text{Fe}(n,p)^{56}\text{Mn}$ reaction. The γ -rays used to identify Fe in the spectrum are 846 keV, 1810 keV and 2113 keV full-energy peaks. The spectrum is presented in Fig. 1. The identification of Al was done by identifying the 1368 keV γ -ray from the decay of the isotope of sodium, ^{24}Na , which is one of the γ -rays with a high intensity (I_γ) of 99% [11]. The other two elements in the mixed metals sample, Ni and Zn, were not easily identified from the background contribution of the reported spectrum. The activation of water CRM and the environmental water sample (Art-Road soil sample) did not show any recognizable γ -ray peaks above the background. The water CRM contained 22 elements which were all present in the order of parts per billion, and this was suspected to be one of the reasons why the water CRM sample was not activated. The spectra of the water environmental sample and that of the water CRM are superimposed in one plot in Fig. 2, where it can be seen that the peaks are mostly background peaks.

Following the results from the irradiation of samples using the STNG, the then remaining samples were irradiated using the Am-Be source. The irradiation of the soil CRM using the Am-Be source in the collimator resulted in the activating of Al. The soil CRM contained 29 elements present in parts per million (ppm) concentration. Al was identified in the soil CRM via the 1368 keV and 2754 keV γ -ray peaks from the decay of ^{24}Na ; this indicating that Al was activated by the fast neutron region of the Am-Be source. The spectrum resulting from the soil CRM was superimposed to the background spectrum in order to identify peaks that are non background contribution.

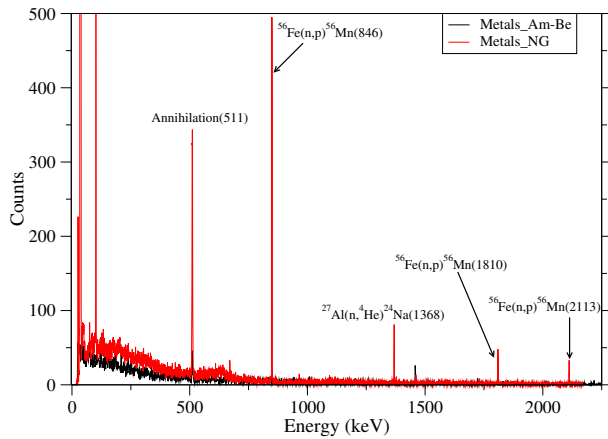


Figure 1. Superimposed spectra of the mixed metals sample.

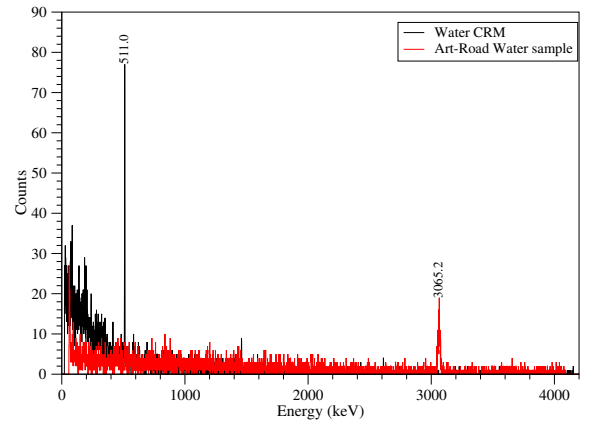


Figure 2. Spectrum of environmental water sample (Art-Road water) irradiated with the STNG superimposed to the spectrum of the water CRM.

The environmental samples that were irradiated using the Am-Be source were dominated by background contribution, and peaks of interest count rates that were too low. The spectra of environmental soil and water samples from Esikhawini are shown in Fig. 3 and Fig. 4, respectively. The spectra of environmental soil and water samples from Mzingazi are shown in Fig. 5 and Fig. 6.

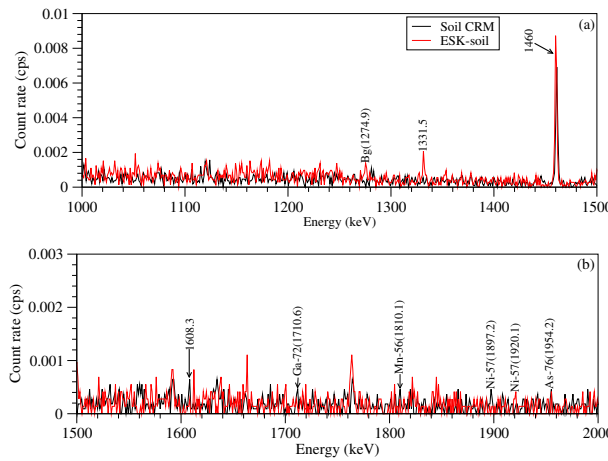


Figure 3. The spectrum of Esikhawini soil sample superimposed to the soil CRM spectrum. The figure shows only the 1000-2000 keV region of the two spectra.

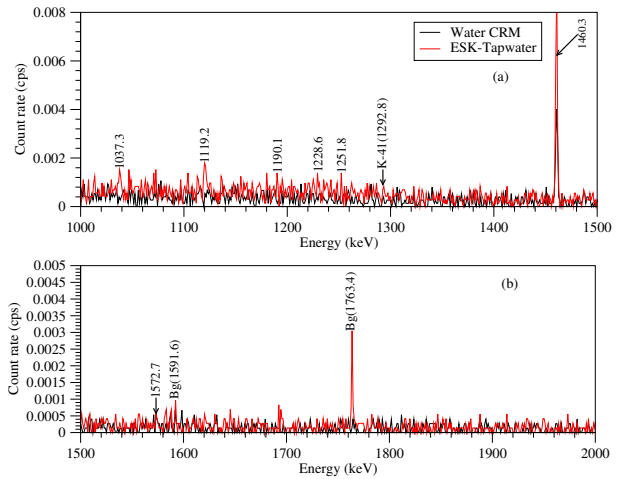


Figure 4. Spectrum of Esikhawini tap water sample (ESK-Tapwater) superimposed to that of the water CRM. The figure shows only the 1000-2000 keV region of the two spectra.

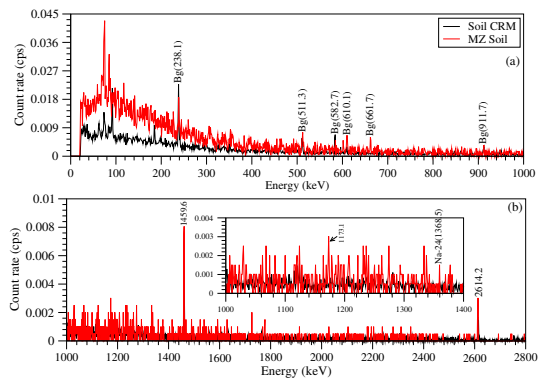


Figure 5. The spectrum of Mzingazi soil sample (Mz-soil) superimposed on the soil CRM spectrum. The figure shows only the 1000-2000 keV region of the two spectra.

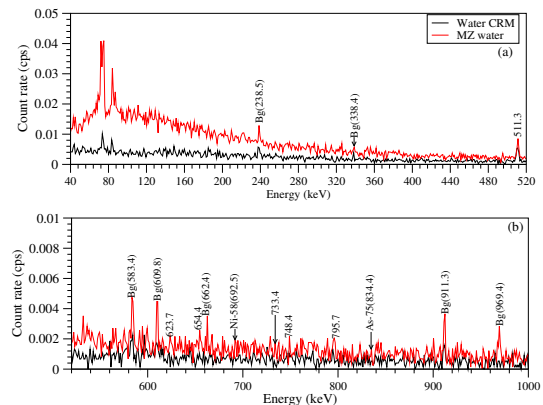


Figure 6. Spectrum of Mzingazi water sample (Mz-water) superimposed on that of the water CRM. The figure shows only the 1000-2000 keV region of the two spectra.

4. Conclusion

The spectra of the mixed metals irradiated at the facility shows that 14 MeV neutrons can be used to analyze for Al. Since it was possible to activate Al in the soil CRM, it is concluded that the facility is capable of identifying the presence of Al at these concentration levels, when using the Am-Be source. The elements in the water CRM sample could not be activated and this is due to the elements being present in parts per billion. This leads to the conclusion that the elements concentration should not be lower than parts per million in a sample. The environmental sample spectra shows peaks from ^{75}As and ^{65}Ni , but the peaks of these γ -ray energies had very low counts and could be due to electronic noise. Further more, the elements of interest could not be identified from the environmental sample spectra. The identification of Al from the soil CRM gives an indication that it can be analyzed using the Am-Be source.

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