

Investigating the feasibility of using neutron activation to measure elemental pollution in the Richards Bay area

Sizwe Mhlongo^{1,2}, Sifiso Ntshangase¹, Peane Maleka² and Ntombizikhona Ndlovu²

¹Department of Physics, University of Zululand, Private Bag X1001, KwaDlangezwa, 3886, KwaZulu-Natal, South Africa

²Department of Subatomic Physics, iThemba LABS, PO Box 722, Somerset West 7129, South Africa

E-mail: sizwesmhlongo@gmail.com

Abstract. Neutron Activation Analysis (NAA) is among the most reliable analytical techniques that can be 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 period of 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 the NAA technique for routine analysis as a result of industrial pollution in the Richards Bay area, Kwa-Zulu Natal, South Africa. Richards Bay is an industrialized area and consists of industries that can potentially release elements such as aluminum, iron, lead, arsenic and others. Experiments with a test sample of mixed metals were made at the facility prior to analyzing the collected samples and they revealed that Al and Fe could be determined accurately with D-T generator, while the Am-Be source was sensitive to Al.

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. The area of Richards Bay is heavily industrialized and there is a possibility of contamination due to industrial activities.

Richards Bay is located in the Northern coast of KwaZulu-Natal, South Africa. The town is one of the industrialized areas in the country; the available heavy industrial activities in the

area include aluminium smelting, a phosphate fertilizer plant, sand dune mining, a kraft-process paper-mill and coal mining [5]. All the mentioned industries have typical elements associated with the waste they produce. Phosphate fertilizer industries may release cadmium (Cd), zinc (Zn) and strontium (Sr) into the environment; aluminium smelting activities may release aluminium (Al), lead (Pb), iron (Fe) and manganese (Mn), while a Kraft process paper-mill industry may release sulfur (S) and chlorine-based compounds [6, 7, 8]. The presence of these industries thus necessitates the need for routine soil and water elemental analysis as a means to monitor elemental contamination in the environment; only a few of such studies have been conducted in the area, with the most recent being in 2016 [9]. The analytical method used by Masok et. al. [9] was the method known as the inductively coupled plasma mass spectrometry (ICP-MS). In this study the aim is to investigate the feasibility of using the NAA in the area to measure the above mentioned elements, which can accumulate in the environment due to the available industrial activities. The motivation behind the choice of NAA is that it has many advantages over most of the commonly used analytical methods. Some of the advantages of the technique are that it is relatively fast and the samples are not destroyed during analysis. This makes it possible to analyze samples multiple times with NAA, or with other methods to benchmark the attained NAA results [1, 2]. Furthermore, although it is not the first time that the technique is used to conduct a study in the area [10], but it has never been used for the purpose of measuring environmental pollution, which makes this study a first attempt to do so.

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 drinking water tap in Esikhawini township using 500 mL polyethylene bottles. Soil samples were collected next to the water bodies and one from one of 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 [1]. 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 9.0651 % of Al, 27.0174 % of Fe, 23.5691 % of Zn and 40.3484 % of nickel (Ni) was prepared inside a glass sample holder and was used for test runs in order to determine the elements the facility would be more sensitivity to.

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 [11]; the neutron facility was commissioned in 2017 with just the STNG [12]. 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 [12]. The STNG is placed inside a vault where it is shielded with high density polyethylene blocks and beads.

The Am-Be source was initially stored inside a box with dimensions of 150cm×150cm×150cm, in which some of the samples were irradiated. The source has since been moved to the same vault 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 of 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 [11]. 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 vault where the STNG is installed. 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 using γ -rays from ⁵⁶Mn, a radioactive product resulting from the ⁵⁶Fe(n,p)⁵⁶Mn 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 through the 1368 keV γ -ray from the decay of the isotope of sodium, ²⁴Na,

which is one of the γ -rays with a high intensity (I_γ) of 99% [13]. 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 (ppb), 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 dominated by background contribution.

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 activation of Al. The soil CRM contained 29 elements present in parts per million (ppm) concentration levels. 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.

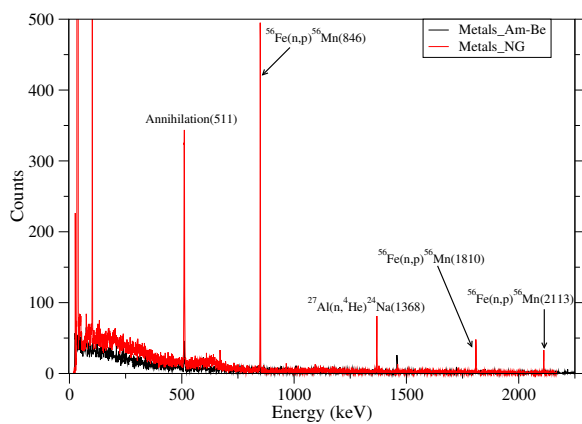


Figure 1. Superimposed spectra of the mixed metals sample.

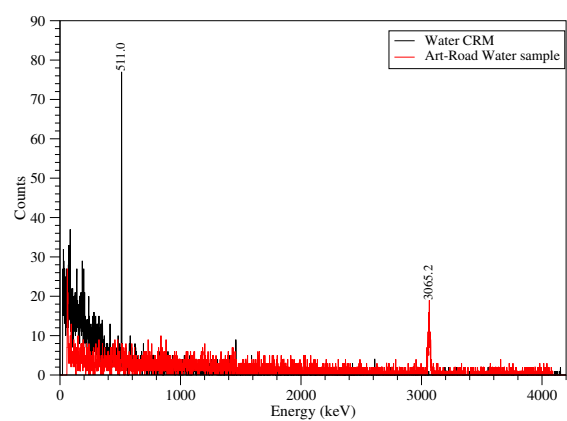


Figure 2. Spectrum of environmental water sample (Art-Road water) irradiated with the STNG superimposed to the spectrum of the water CRM.

The environmental samples that were irradiated using the Am-Be source were dominated by background contribution, and peaks of interest with very low count rates. As a result, the analysis procedure did not reach the quantification stage. Furthermore, even if there were high count rates for the energy peaks of interest, it was still not going to be possible to quantify the elements using the comparator method, since the suspected peaks were not present in the CRMs. As explained under the experimental method section, the quantification of elements using the comparator method requires that the elements that are being analyzed for must be present in the CRM as well, and must be activated in both the sample and CRM under similar experimental conditions. 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.

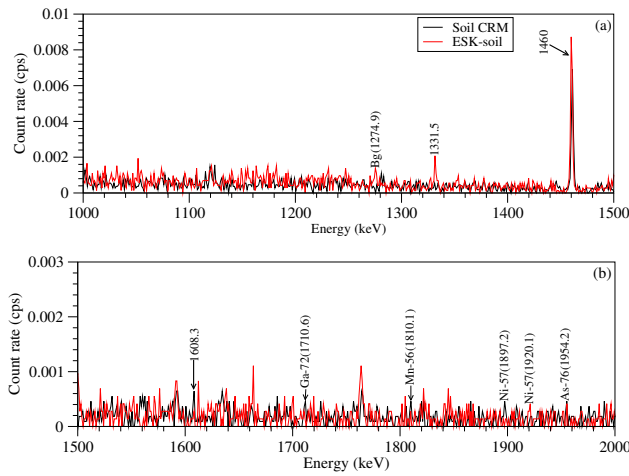


Figure 3. The spectrum of Esikhawini soil sample superimposed to the soil CRM spectrum. The figure shows only the 1000-2000 keV region of the two spectra.

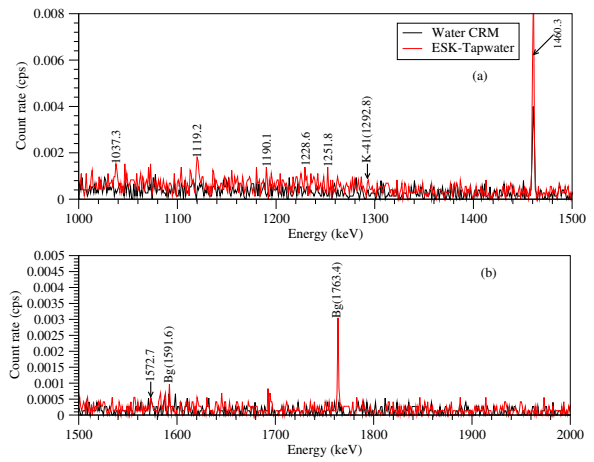


Figure 4. Spectrum of Esikhawini tap water sample (ESK-Tapwater) superimposed to that of the water CRM. The figure shows only the 1000-2000 keV region of the two spectra.

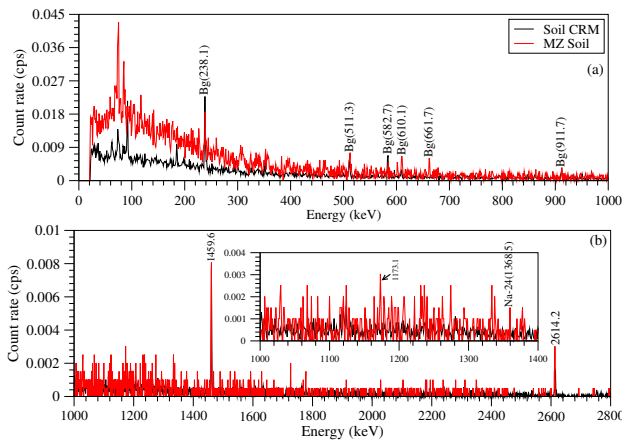


Figure 5. The spectrum of Mzingazi soil sample (Mz-soil) superimposed on the soil CRM spectrum. The figure shows only the 1000-2000 keV region of the two spectra.

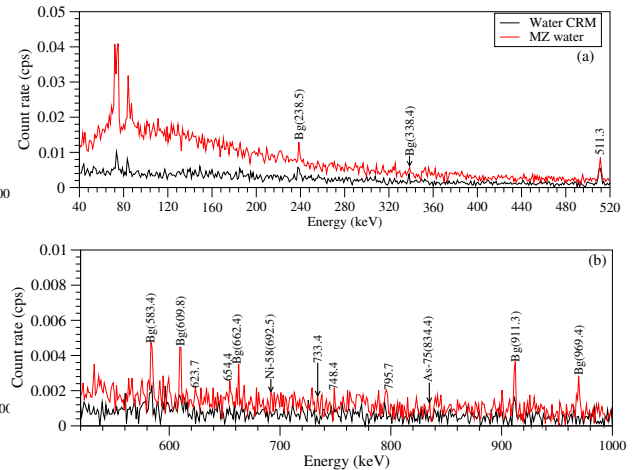


Figure 6. Spectrum of Mzingazi water sample (Mz-water) superimposed on that of the water CRM. The figure shows only the 1000-2000 keV region of the two spectra.

4. Conclusion

The spectra of the mixed metals irradiated at the facility shows that 14 MeV neutrons can be used to analyze for Al and Fe using high intensity γ -rays from ^{24}Na and ^{56}Mn , respectively. However, the successful activation of Al and Fe is attributed to the fact that they were present in high concentrations. Since it was also possible to activate Al in the soil CRM, this meant that the facility is capable of identifying Al present in ppm concentration levels using the available Am-Be source. However, Fe was not successfully activated even though it was present in the CRM. Thus, a conclusion that can be drawn from this study is that the use of the technique is feasible for Al analysis in soils using fast neutrons from the neutron facility at UCT. For other elements of interest, there is a need for further studies as it is suspected that they were present in concentration levels that are below the limits of detection of the facility. This is

mostly true for the elements in the water CRM, in which they were present in ppb concentration levels. The challenges of sensitivity can be overcome through employing other types of NAA, such as those involving chemical separation; alternatively, a different neutron facility with high sensitivity to the elements of interest can be used.

5. Acknowledgements

This work is supported by the University of Zululand and the National Research Foundation (NRF), through the MANUS/MATSCIE program, iThemba LABS and under grant number 106012. The authors also wish to thank the following people for their contribution to this work: Dr. Tanya Hutton, Prof. Andy Buffler, Mr. Michael Van Heerden (Department of Physics, UCT) and Mr. Graham Daniels (NECSA).

References

- [1] Kharfi, F. L. (Ed), 2013, *Imaging and Radioanalytical Techniques in Interdisciplinary Research - Fundamentals and Cutting Edge Applications*.
- [2] Guinn, V.P. and Hoste, J., et al., 1980, *Analytical Techniques For Trace and Minor Elements in Biological Materials: Current Problems and Techniques. With Special Reference to Trace Elements*, iaea.org, viewed on 4 February 2017 from http://www.iaea.org/inis/collection/nclcollectionstore/_public/-11/564/11564331.pdfpage=115.
- [3] Chadwick, J., 1932, "Possible Existence of a Neutron", *Nature* 129, 312.
- [4] Mulhauser, F. (ed), "Neutron Generators for Analytical Purposes", Vienna, 2012, International Atomic Energy Agency, IAEA.
- [5] Okello, N. & Allan, C., 2015, "The Richards Bay Clean Air Association: A Case Study for Success in Participatory Air Quality Management", *The Clean Air Journal* 25(1), 35 – 37, viewed on 4 February 2017, from http://www.cleanairjournal.org.za/download/caj_vol25_no1_2015_p34.pdf.
- [6] Rotimi, A., Umo N. et al., *Environmental Pollution Induced by an Aluminium Smelting Plant in Nigeria*, researchgate.net, viewed on 19 May 2017, from www.researchgate.net/publication/268265647_Environmental_Pollution_induced_By_an_Aluminium_Smelting_Plant_in_Nigeria.
- [7] Mumford, M. & Engelhardt C n.d., "Pulp and Paper mill Pollution Effects on Estuarine Environments", Coastal Carolina University, Conway.
- [8] Kassir, L., Lartiges B. et al., *Effects of Fertilizer Industry Emissions on Local Soil Contamination: A case study of a phosphate plant on the east Mediterranean coast*, iahr.tandfonline.com, viewed on 19 May 2017, from www.iahr.tandfonline.com/doi/abs/10.1080/09593330.2011.601765.
- [9] Masok, F.B., Masiteng, P.L., Mavunda, R.D. and Maleka, P.P., 2016, "Chemical Contamination and Radiological Risk Assessment of Water Sources in Richards Bay", *Journal of Physical Science and Application* 6(5).
- [10] Masok, F.B., Masiteng, P.L., Mavunda, R.D. and Maleka, P.P., 2016, "Health Effects Due to Radionuclides Content of Solid Minerals within Port of Richards Bay, South Africa", *Int. J. Environ. Res. Public Health*, 13, 1180.
- [11] ThermoFisher Scientific n.d., Thermo Scientific MP 320: Lightweight, Portable Neutron Generator, viewed 14 April 2019, from <https://www.thermofisher.com/order/catalog/product/1517021A>.
- [12] Hutton, T, and Buffler, A., 2017 *J. Phys.: Conf. Series* 62 324330.
- [13] Chu, S.Y.F., Ekstrom, L.P. and Firestone, R.B., computer software, viewed March 2018 from <http://nucleardata.nuclear.lu.se/toi/index.asp>.