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Validation of alpha spectrometric analytical measurement procedure for the determination of Polonium-210 (^{210}Po) in environmental samples

Master's Thesis

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ABSTRACT

Polonium -210 (^{210}Po), a low activity alpha radioactive element can have an impact on human health as a results of internal contamination due to its high radiotoxicity when handle improperly. The wide spread of ^{210}Po in the environment due to it source; daughter product of uranium (^{238}U), it is very essential to have a measurement procedure to monitor and access it activity concentration levels.

This thesis therefore aims at finding suitable alpha spectrometry measurement procedure and validating it to be implemented in the laboratory where it can be used for routine analytical procedure for the determination of ^{210}Po in environmental samples.

In establishing if the procedure is fit for it intended purpose, the following validation parameters will have to be determined; trueness, accuracy (En-value, z-score), relative bias, and tracer recovery. Also establishing the main sources of uncertainty and their percentage contribution.

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1 INTRODUCTION

The growing awareness on the potential hazards of radioactivity has resulted in an increasing concern with regard to mining, manufacturing and it related industries where radioactive materials are generated. Such industries include nuclear power plant (PP's),fossil fuel PP's,fertilizer manufacturing and constructional material.Living organisms have the potential to come in contact with radioactive materials from natural sources such as the soil and the Earth's crust. Additionally,in some locations the level of radioactivity is elevated due to technological processes [1].

The level of radiation generated plays an important role in the determining its effect on human health and environmental sustainability. Exposure to ionizing radiation which exceeds recommended levelscan be hazardous to human health[2]. National regulatory authorities and international organizations such as International Atomic Energy Agency, (IAEA) provide guidelines on the recommended levels can cause health problems such as cancer, birth defects and even can result in death[3].

In properly controlled and monitored radioactive may have long-term negative impact on the environment, since some radionuclides have half-life equal to millions of years. This makes it important to engage in research and development projects and activities.For example, naturally occurring radioactive material (NORM) may be present a continuous concern if the threats associated with it addressed properly.

The new Basic Safety Standard (EURATOM 2013/59) indicates that European Union member states should consider natural sources of radioactivity clearly states that natural radiation sources should be considered equally with anthropogenic sources, while identifying industries with potential for radiation hazard[4].

The thesis will focus on the sample preparation stages of the analytical procedure, since these form the most sensitive part of the measurement procedure. These include ensuring the analyte is separated well and avoiding contamination and loss of analyte. The aim is to optimizesample preparation parameters forimproved recovery of the analyte before alpha spectrometric measurement.

This thesis report is divided into six chapters. The first three chapters consist of the theoretical component of the work. Chapter one is introduction. Chapter two is the literature review and provides detailed information about the radionuclide ^{210}Po, various sample preparation methods, alpha spectrometric techniques, and validation parameters for the analytical measurement procedure. Chapter three offers anin- depth analysis of the procedures used, explaining the order of steps used in the analytical measurement procedure. Chapter four demonstrates how the measurement procedure is carried out for different certified reference materials and present the experimental work results and discussion. Chapter five is dedicated to conclusions and recommendations. Finally, chapter six includes to all the references used.

2 LITERATURE REVIEW

2.1 Polonium-210

Polonium-210 (^{210}Po) is a naturally occurring radioactive isotope. It is one of the 25 known isotopes of polonium with atomic mass of 209.0 atomic mass unit (amu). This silvery-gray element dissolves in dilute acids, but it is only slightly soluble in alkalis. It has very low concentration in the environment as a part of the uranium-238 decay chain. This can be derived from lead-containing wastes from uranium, vanadium, and radium refining operations. It may be also produced artificially, which requires fairly sophisticated equipment especially used in the nuclear industry[5][6].

Marie Curie Polish-French scientist discovered Polonium in 1898 and it was dedicated after her birthplace in Poland. Curie achieved this by her attempt to look for the source of radioactivity in a naturally occurring ore called pitchblende. It required several tons of pitchblende to yield very small amounts Polonium, obtainable value of about 10-6 g per ton of ore.Polonium could be considered as the heaviest element in the chalcogen family. It is found in Group 16 (VIA) on the periodic table[5][7].

Polonium-210 is regarded as naturally occurring radionuclides with a wide distribution where there is a high potential for human exposure as a result of inhalation or ingestion. It is also considered as one of the naturally occurring radionuclides that is most toxic[8]. Polonium-210 is the main contributor radioactivity found in human foodstuffs [9].

2.1.1 Sources of Polonium

Polonium -210 as a naturally occurring radionuclide with a half live of 138.376 ± 0.002 days[10]. The main environmental source of ^{210}Po is from uranium-238 decay chain which is distributed in the Earth crust.Atmospheric and natural water source of polonium is a result of^{22}Rn emanation which is released from the earth's crust to the atmosphere[11]. Artificially, polonium source could be enhanced from activities disposal of radium –rich materials and also from mining waste (tailings and effluents) generated in uraniferous rich areas [11].

2.2 Polonium -210 sample preparation method

There are various sample preparation methods such as acid digestion in a pressure vessel, wet ashing in open system and microwave assisted digestionfor determination of polonium-210 content in a given sample.This sample could be in as original form of the sample is in liquid or solid before auto-depositing /plating on a suitable metal plate for alpha spectrometry measurement[12]&[11]. Below are some of the sample preparation techniques commonly used for ash and soil samples.

2.2.1 Mineral and organic samples

The initial sample preparation stages for soil, sediments and fly ash involves both physical and chemical processes. Mostly the physical process depending on the nature of the sample may include grinding, drying at a suitable and regulated temperature due to volatile nature of polonium. Significant losses can occur when applying temperatures over 100 degreesCelsius[10].The chemical process encompasses sample dissolution and chemically aided process for organic matter destruction.

There are various solid sample dissolution techniques for extracting the analyte from its associated matrix. The common and main methods that are used for dissolving the sample include; microwave assisted digestion, wet ashing in an open system and also digestion in a pressure vessel[13].

2.2.1.1 Wet ashing in an open system and digestion in pressure vessel.

This method is used to extract the analyte (polonium) from the inorganic matrices or the oxidizing the organic part of the samples with the use of suitable concentrated acids or mixtures. The commonly used acids include mixtures of HF, $HClO_4$ HCl, or HNO_3.These reagents suitable for soil and sediment samples[13]. This method has some disadvantages with its operation such as the possible risk of sample contamination from external sources especially when handling [210]Po activity concentration at trace level from a sample, time-consuming process and analyte lost when the temperature variation is not well monitored. Challenges such as temperature limitation and possible volatilization of polonium-210, operating with closed pressure vessel helps solve these limitations. Additionally, it helps increase the reaction kinetics of the process [13].

2.2.1.2 Microwave assisted digestion system

Microwave assisted digestion method offers digestion/decomposition of both inorganic and organic matrices associated with the element of interest under controlled conditions. This method was introduced to achieve as much as possible complete decomposition of the solid matrix while preventing loss or contamination of the analyte. Similarly, acids and/or mixtures such HF, $HClO_4$ HCl, HNO_3, are used for the process. This thesis focus on the initial stages of the sample preparation for dissolution and freeing the analyte as much as practicable from it matrix using microwave assisted digestion system is much better alternative due to the follow merits[14][15].

➢ Time saving;it is made possible for many samples to be digested simultaneously and reaction times are typically less in comparison to open digestion method.

➢ Acid consumption is lower in microwave digestion and reduced exposure of analyst to corrosive acid fumes as compared open digestions.

➢ Microwave digestion systems offer greater extraction efficiency whereas in open system digestion extraction can be incomplete depending on discretion of the analyst.

➢ A greater risk of contamination from external sources exists in open digestion whereas in closed systems the risk is non-existent and loss of volatile elements is reduced.

Microwave assisted digestion systems has a main drawback due to the possible explosion and cracking of digestion tubes as a result of simultaneous build – up of pressure fromwith increasing temperature. However, microwave systems have a safety inbuilt sensors for both temperature and pressure in ensuring that it operates within the set limit. The microwave power is automatically controlled or shut-off when pressure reaches the maximum limit.

Microwave assisted digestion system advantages far outweigh the disadvantage and is therefore a very useful addition to high throughput laboratories [15]

2.3 Alpha spectrometry

Alpha spectrometry operates by measuring the energy of the alpha particle emitted in the decay radionuclides where count rates are converted into activity concentration values.

Alpha decay is regarded as a type of radioactive disintegration during which unstable atomic nuclei dissipate excess energy by spontaneously ejecting an alpha particle. Because alpha particles consist two positive charges and a mass of four units, their emission from nuclei produces daughter nuclei having a positive nuclear charge atomic number two units less than their parents and a mass of four units less.

The speed and hence the energy of an alpha particle ejected from a given nucleus is a specific property of the parent nucleus and determines the characteristic range or distance the alpha particle travels. Though ejected at speeds of about one-tenth that of light, alpha particles are not very penetrating. Half-lives for alpha decay range from about a microsecond (10^{-6} second) to about 10^{17} seconds [14].

2.3.1 Applications

Alpha spectrometry could be considered as a very sensitive technique with a very low counting background. Alpha spectrometry serves as an appropriate technique applied to radioanalytical operations due to its versatility, low background, high detection efficiency and high sensitivity. In addition, the use of an alpha-emitting isotope as an internal tracer such as polonium-209 makes it a highly reliable measurement procedure[16].Environmental sample with lower activity concentration could be measured using alpha spectrometry measurement.

2.4 Validation

Validation is the process used to experimentally confirm that the analytical procedure for a specific test is suitable, reliable and valid for its intended use. Results from validation can be used to checking the analytical procedure, determine the quality, reliability and consistency of results; it is an integral part of any good practice. Therefore, carrying out validationfacilitate in ensuring that analytical procedure parameters are monitored for validity and suitability in accomplishment of the proposed use of the analytical procedure.

2.4.1 The importance of validation for analytical procedure

The results from measurements is very important for decision making regarding every aspect of life such as human health and safety, environmental matters. For instance, measurement results help authorities make informed decision and maintaining standards.

This fully required needed evidence to support the measurement procedure used in obtaining the results.

The biggest advantage of analytical procedure validation is that it builds a degree of confidence, not only for the developer but also to the user. Although the validation exercise may appear costly and time consuming, it results is inexpensive, eliminates frustrating repetitions and leads to better time management in the end.

Minor changes in the conditions such as reagent supplier or grade, analytical setup are unavoidable due to obvious reasons but the method validation absorbs the shock of such conditions and pays for more than invested on the process[17].

2.4.2Validation parameters

Validation parameters/characteristics for ensuring that the analytical procedure is fit for purpose include;under listed are some of the validation parameters[18].

Trueness; isthe closeness of agreement between the average values obtained from a large set of replicate test results and an accepted reference quantity value.

Accuracy; is described as the closeness of agreement between a measured quantity value and a true quantity value of a measurand. And may be classified as equal to the addition of trueness and precision.

Precision;this is an analytical procedure used to express the closeness of agreement between a series of measurements obtained from multiple sampling of the same homogenous sample.It is usually expressed as the standard deviation (S) or coefficient of variation (RSD) of a series of measurements.Precision may put into these main components:

- ✓ Repeatability;involves analysis of replicates by the analyst using the same equipment and method and conducting the precision study over short period of time while. Repeatability is also termed intra-assay precision [19]&[20].

Specificity is the ability to assess unequivocally the analyte in the presence of components which may be expected to be present. These could include impurities and matrix during the sample preparation and measurement process[21].

Robustnessof an analytical procedure is a measure of its capacity to remain unaffected by small, but deliberate variations in method parameters and provides an indication of its reliability during normal usage [21]

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3 ANALYTICAL PROCEDURE

3.1 Description of procedure

Alpha spectrometric measurement of Polonium- 210 activity concentration applicable to environmentalsample is the caption for this measurement procedure. This was achieved by using reference materials to the analysis the procedure.

The measurement procedure outlines the steps involves starting from sample preparation stages through auto- deposition on a suitable metal disc to alpha spectrometer measurement and finally spectrum analysis. The outline includes this main parameter such as sample preparation, measurement steps, establishing traceability associated to the analytical measurement procedure.

3.1.1 Measurand, analyte and units

Measurand is the quantity that is intended to be measured. The measurand in this case is to measure the activity concentration of polonium-210 in the reference samples. The unit used for this measurement procedure are presented or converted to Becquerel per kilogram of the sample (Bq/kg).

3.1.2 Apparatus /equipment and reagents used

These include the main standard equipment and regents needed in ensuring an efficient and effective analytical work. Appendix I provides the list of equipment and supplies that were used.

3.1.2.1Reagents

- ✓ Ascorbic Acid.
- ✓ Deionised water. Use in all dilutions requiring water.
- ✓ Ethanol
- ✓ Hydrochloric Acid, 0.5 M.
- ✓ Hydrofluoric Acid, (40% concentration)
- ✓ Nitric Acid, with 65% concentration
- ✓ Standard Tracer- Polonium-209 Solution, obtained from Oak Ridge National Laboratory (USA) with initial activity of 1.0 μCi (For the procedure, dilution was prepared).

✓ Boric acid, saturated solution.

3.2 Analytical Procedure used

Thisprocedure is classified three into main steps. These are sample preparation, spontaneous deposition and alpha spectrometric measurement. The sample preparation is a modified procedure from IAEA () which is sequential steps customized for Ca-rich oil shale and environmental samples
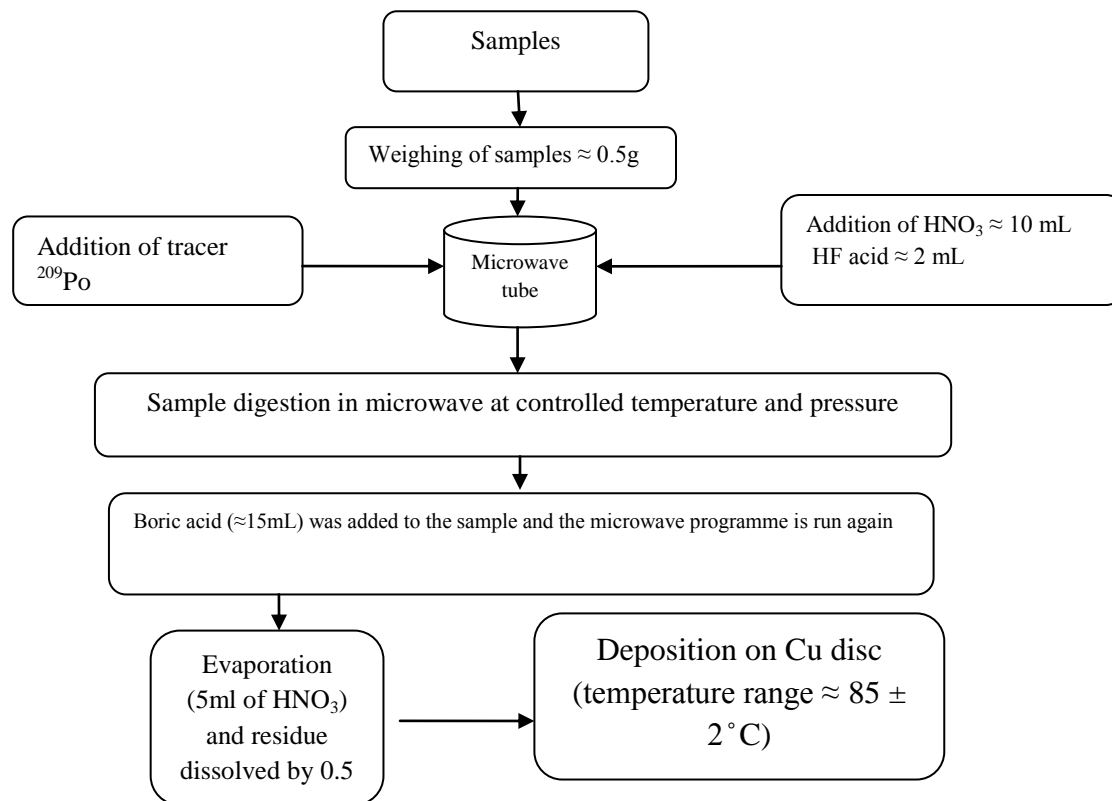
Figure 1: Sample preparation stages

3.2.1 Sample preparation

This is also grouped into drying of sample, weighing and microwave assisted digestion process aimed at liberating the analyte from it associated matrix and getting the sample in solution form.

Drying of sample and weighing:The sample used for this procedure is solid environmental sample, since it may contain some amount of moisture, it important to subject it to drying at control temperature at about 50ºC for 24 hours. The dried sample is homogenized (mixed by gently shaking the container) followed by weighing replicate samples with a precision analytical balance.

3.2.1.1 Microwave assisted digestion process

Due to the nature of samples treated and how the analyte is associated with it matrix, microwave assisted digestion process is used to enhance the dissolution of the sample. The under listed steps show how the microwave assisted program is carried out.

➢ Weigh an amount of about 0.5 g, depending on it activity of the dried sample accurately into the microwave digestion vessel with the use of analytical balance.

➢ Spiking or tracer (^{209}Po) is weighed and added to selected replicate samples for quality control and other validation method determination.

➢ The required concentrated acids are added under a fume hood. That is 10 mL of HNO_3 and 2 mL of HF. The mixture is gently swirl and wait for some time before closing the vessel. It is recommended that the waiting time could be approximately 10 minutes and allow the mixture to stand until any visible reaction had ended and then properly capped [20]&[21].

➢ The vessel containing the mixture is place in the microwave system carefully. Suitable performance program parameters such temperature and pressure are selected to designed to achieve consistent leaching of the sample by achieving specific reaction conditions.

➢ At the end of the microwave set program for the digestion, the vessels are allowed to cool using the cooling system within the microwave instrument. The cooling is also further done under a well-ventilated fume hood. This is to ensure that it cooled before proceeding to the next stage of the digestion process.

➢ The next step is to repeat the microwave digestion process by maintaining the operating parameters.The only difference is the addition of H_3BO_3. This isrecommending to avoid damaging any glassware used during analysis by complexing the excess HF present with a saturated H_3BO_3solution [16]. HF reacts with naturally occurring calcium to form inert calcium fluoride (CaF) (Jaffe et al., 1987).For this reason, boric acid (H_3BO_3) in H2O (saturated solution) was used in order to dissolve CaF precipitation during the first stage of microwave assisted digestion, and to remove the remaining HF from the sample solution.

➢ The same process of cooling is done and then it is quantitatively transferred the digested sample to an empty clean tube.

3.2.1.2 Evaporation to dryness

The digested dissolved sample solution was introduced into Teflon Beaker and followed by evaporation to dryness. The residue from the evaporated sample is dissolved with HCl acid. The evaporation process is carried out within the temperature ranges between 55 to 65 ^{o}C to ensure that the analyte (^{210}Po) is not loss due to the volatility of ^{210}Po

Evaporation to dryness is necessary to get rid of any residual HF acid that was used during the microwave assisted digestion process. This is needed due to the effect on human and laboratory glassware such as glass beakers. Below are short descriptions on the evaporation to dryness process:

➢ The digested sample is taken through centrifugation to ensure it is effective mixing.

➢ Introduced into Teflon beaker and placed on heated plate to evaporate to dryness.

➢ Concentrated HNO$_3$ about 5 mL is added to the dry samples and subjected to evaporation to dryness and this is repeated this two additional more.

➢ The residue from this evaporation process is dissolve with require concentration of 0.5 M HCl acid.

Additionally, before evaporation to dryness, some of the digested samples may contain some precipitate which will need extra sample preparation.
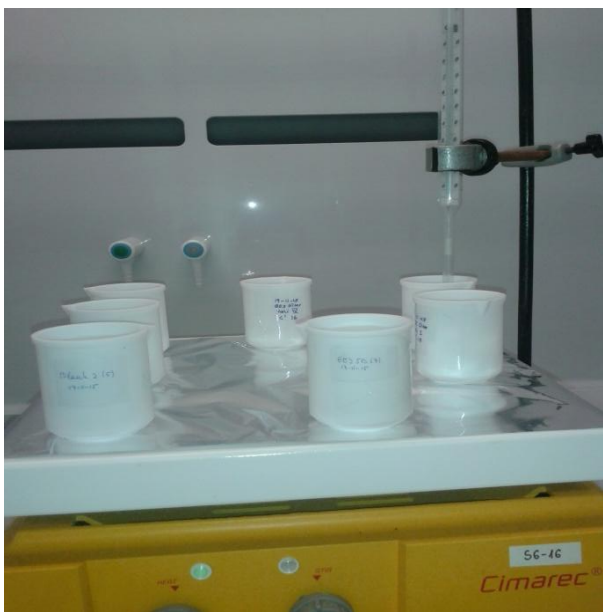
Figure 2: Evaporation to dryness at controlled temperature

3.3 Spontaneous deposition of Polonium-210

The next stage for this analytical procedure is the depositing the polonium-210 onto a suitable metal disc plate due to the solution chemistry of polonium [22].

A Whatman 1 filter paper is used to filter out any residue that might interfere with the deposition process. 0.4 g of ascorbic acid is added to the solution in order to minimize interferences such as iron during auto-deposition. Copper disc is used for spontaneous deposition process [21]. Cleaning of the copper disc is achieved by first gently washing with demonized water, diluted HNO_3 acid and with ethanol and disc allowed to dry. The under listed are the main procedures for the spontaneous deposition process.

- ➢ Filtration sample solution (after evaporation to dryness) with Whatman 1 filter paper with diameter 125 mm in a clean dry glass beaker.
- ➢ The copper disc is held in place in a Teflon holder unit supported by a magnetic stirring bead with one side of the copper plate covered, ensuring that the deposition only occurs at one side of the disc (plate). It is advantageous to deposit on one side of the plate compare to plating on both side of the plate. Because the higher activity concentration the better counts of the acquired spectrum, improved sensitivity, reduced counting time needed and much improved accuracy[22].
- ➢ The prepared plate supported with Teflon holder and a magnetic stirring bead is gently immersed in the filtrate solution contained in the glass beaker.
- ➢ Water bath of temperature around 80 ^{o}C is prepared using 800 mL glass beaker with heating via a rotating hot plate where the glass beaker containing the dissolved sample is placed in it.
- ➢ The spontaneous deposition process starts when the temperature reaches 85 ± 2 ^{o}C and maintained throughout the deposition period (for four hours).
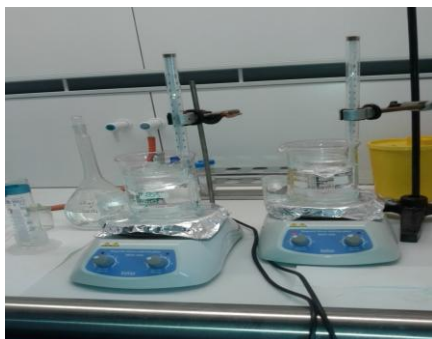
Figure 3: Spontaneous deposition process

3.3.1 Spontaneous deposition control parameters

The main aim of spontaneous deposition is to ensure that as much as possible most of the analyte (^{210}Po) deposited on the plate during the auto-deposition process. It is therefore important to monitor and control operating parameters to obtain an optimum recovery of the polonium for the subsequent alpha measurement. The following main parameters were monitored and adjusted in ensuring the analytical procedure is optimized.

3.3.1.1Acid used for deposition media

The volume and concentration (acidity) of the acid used- Hydrochloric acid is essential in achieving good deposition recovery. HCl concentration of 0.5 M with volume of 80 mL was used which relatively gives better output for the deposition[10].

3.3.1.2Deposition temperature

Temperature serves as an important parameter during the deposition stage. This is due to the volatile nature of polonium. Optimization of temperature is desirable and helps to achieve a good percentage of polonium deposition[22]. In this analytical measurement procedure, the temperature was regulated around 85 ± 2 ^{o}C during the deposition period.

3.3.1.3 Deposition time

Deposition time Optimization for spontaneous deposition of polonium are according Matthews et al. (2007), reduction of the needed deposition time may be achieved by using required high temperature, small solution volume with agitation of the solution, where acid strengths of solution pH ranges from 1.5 - 2. Various variations with deposition time while maintaining the other deposition parameters. The most suitable time duration for this procedure is 4 hours of deposition.

3.4 Alpha spectrometric measurement

Alpha spectrometry is a sensitive technique was to analyze alpha emitting radio- isotopes with the help of semiconductor detector spectroscopy. This makes it effective for the measurement of ^{210}Po by alpha spectrometry with detectors such as silicon surface barrier or PIPS detectors, mainly due to their excellent energy resolution, compact size, low background, excellent stability and low sensitivity to γ-radiation.Generally, an alpha spectrometry system is set up to generate spectra alpha energy range between 4 and 10 MeV.

3.4.1 Spectrometry features

The alpha spectrometer used for this alpha measurement has the following important features which help within the effective operation of the instrument.

➢ Stainless steel vacuum chamber

➢ Built-in counter/timer

➢ Bias supply variable

➢ Integral vacuum gauge with vacuum

Also comes with a digital display such as;

➢ Counter/Timer

➢ Chamber Pressure

➢ Detector Bias

➢ Leakage Current

3.4.2 Parameters related to alpha spectrometry

Optimization and selection of suitable parameters associated to the alpha spectrometry plays an important role for alpha particle measurement. Parameters considered include detector, source of vacuum, distance.

3.4.2.1 The Alpha spectrometer detector and vacuum of the detector chamber

The vacuum of the detector chamber is maintained at less than 100 mTorr before the bias is turn on and also it is usedthroughout the counting process using a high efficient vacuum pump.It is very important to create a vacuum for alpha spectrometer measurement because the range alpha particles are readily absorbed in air in just some few distance and as well as its energy degrade significantly in a few millimeters, therefore measurement is done in vacuum to prevent any interaction with the air before it reaches the detector.

3.4.2.2 Counting efficiency and source-detector distance

The alpha spectrometer efficiency was determined based theoretically calculated formula [from excel]from disc source to detector distance. With low activity measurements mostly applicable to environmental samples. This makes counting efficiency an important parameter to consider. According to Hendee, 1984[23], if a disc source of

radius **a** counted at a distance **h** from the detector of radius **r**, the counting efficiency could be calculated as

$$E = 0.5 * \left(1 - \frac{h}{\sqrt{h^2+r^2}}\right) - \frac{3}{16}\left(\frac{ar}{h^2}\right)^2 \left(\frac{h}{\sqrt{h^2+r^2}}\right)^5 \qquad\qquad \text{Eqn (1)}$$

Measurements using the alpha spectrometer were made at two different levels, which is the distance between the detector and where the auto-deposited copper is held in place for measurements. Figure 4 shows the positions of the detector and the movable sample holder.
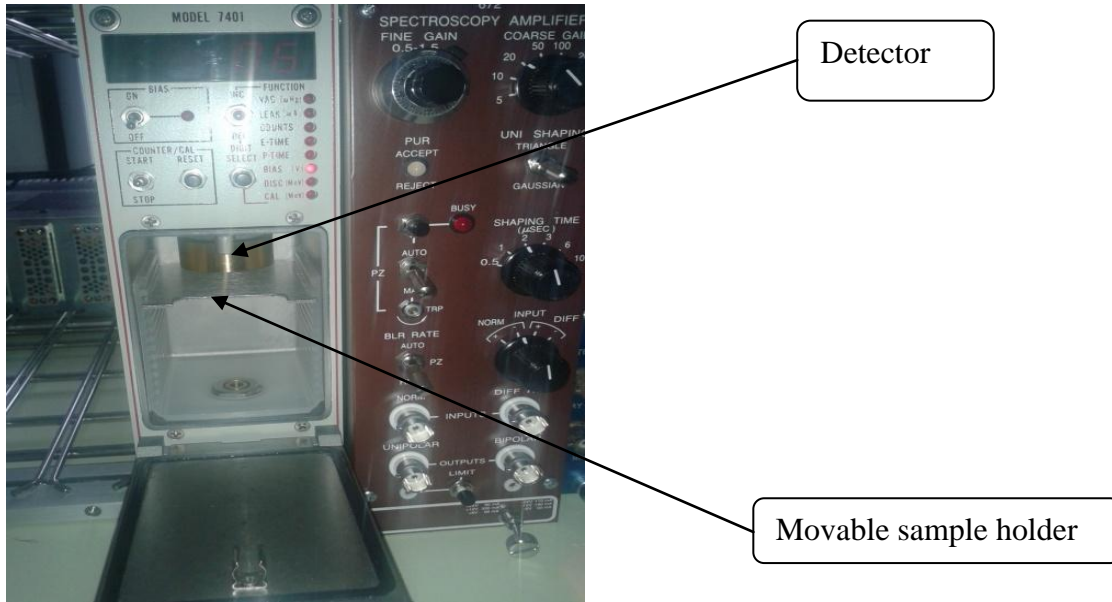
Figure 4: Position of detector and movable holder

3.4.3 Data acquisition and spectrum analysis

Data acquisition from the measurement procedure involves the process of obtaining the basic information from the alpha spectrometric measurement made. This serve as the initial foundation in evaluating the activity concentration of the analyte (polonium -210) in the sample and main contributing uncertainties from the analytical procedure. Figure 5 is an example of spectrum obtained from measuring a sample with a tracer.
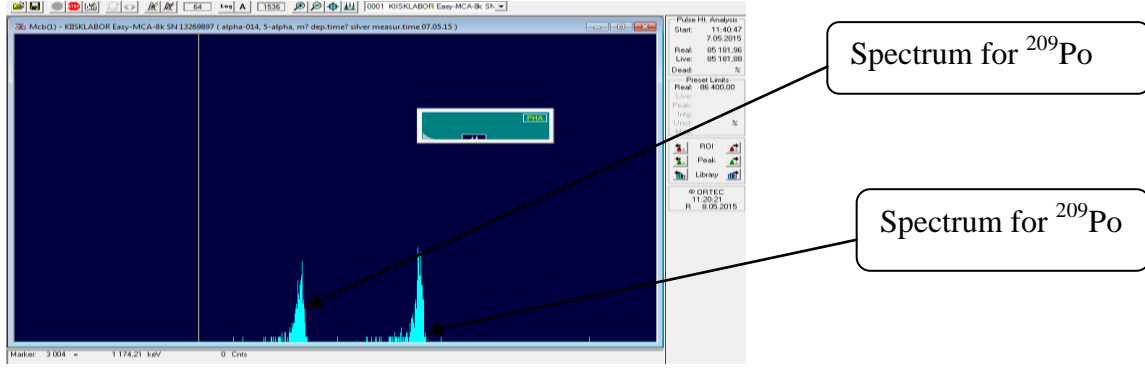
Figure 5: An example of spectrum for ^{209}Po and ^{210}Po

Below are main steps used for the evaluation in establishing the concentration and its associated uncertainties.

3.4.3.1 Calculating Activity

The activity was calculated based on activity per unit mass of the sample, although it is possible to have the evaluation of the activity as activity per unit volume of the sample. The main reason being that because weighing helps reduce the uncertainty budgets associated in getting the amount of sample for the analytical process. Therefore, for each energy in the alpha spectrum obtained from the measurement, the activity per unit mass C_A, on the sample date -decay corrected estimation according to IAEA-TECDOC 1401, 2004) underlisted equations[24];

$$C_A = \frac{A_A}{m_s * q} * f_1 * f_2 * f_3 * f_4 \qquad \text{Eqn (2)}$$

Also A_A is evaluated below

$$A_A = C_T * m_T \left[\frac{R_{GA} - R_{BA}}{R_{GT} - R_{BT}} - q_1 \right] \left(\frac{P_{\alpha T}}{P_{\alpha A}} \right) \qquad \text{Eqn (3)}$$

$$f_1 = e^{(+\lambda_A * (t_s - t_E))} \qquad \text{Eqn (4)}$$

$$f_2 = \frac{\lambda_A * t_G}{1 - e^{(-\lambda_A * t_G)}} \qquad \text{Eqn (5)}$$

$$f_3 = e^{(-\lambda_T (t_s - t_c))} \qquad \text{Eqn (6)}$$

$$f_4 = \frac{\lambda_T * t_G}{1 - e^{(-\lambda_T t_G)}} \qquad \text{Eqn (7)}$$

➢ A_A – Activity of the analyte, ^{210}Po on the deposited copper disk

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- m_T – mass of the tracer
- m_s – mass of sample
- R_{GA} – Gross counting rate of the analyte with counting time T_G
- R_{GT} – gross counting rate of ^{209}Po with counting time t_G
- R_{BT} – Blank counting rate for tracer, with counting time t_B
- R_{BA} – Blank counting rate of analyte
- q_1- isotopic impurity ratio of ^{210}Po in the tracer solution.
- $p_{\alpha T}$ – sum of the alpha emission probabilities for ^{209}Po region of interest
- $p_{\alpha A}$ - sum of the alpha emission probabilities for ^{210}Po region of interest
- f_1 – correction for decay of ^{210}Po from sampling to measurement
- f_2 – correction for decay of ^{210}Po during the interval period t_G
- f_3– correction for decay of ^{209}Po from its calibration date to measurement
- f_4 – correction for decay of ^{209}Po during the counting interval of the gross counting (in seconds).
- t_s – start of the measurement time
- t_c – time of calibration of ^{209}Po solution
- t_G – counting time interval of the gross in seconds (s)
- λ_T – decay constant of ^{209}Po in s^{-1}
- λ_A– decay constant of the analyte, ^{210}Po in s^{-1}
- q_1 – isotopic impurity ratio of polonium isotope in the tracer solution
- C_T – certified activity concentration of the tracer solution

3.4.3.2 Minimum detectable activity

This is regarded the lowest amount of activity which is distinguishable from the background which can be reliably quantified at a given confidence level mostly 95%[24]&[25] With alpha spectrometric analysis, the MDA will depend on some parameters such as:

The energy of the analyte (radionuclide) to be determined.

- The level of detector sensitivity.
- The possible presence of contaminants with similar radiation energy. This mostly depend on the nature of the analyte to be measured and quantified [24]

MDA is obtainable from the measurement from Eqn 8[26].

$$\text{MDA}= \frac{4.66*\sqrt{B}+3}{t*E.R} \qquad\qquad\text{Eqn (8)}$$

The tracer recovery, R is obtainable by the equation;

$$R =\frac{N_t}{t.E.A_t} \qquad\qquad\text{Eqn (9)}$$

Where; B - the net area count background, t - Counting time (sec),E - Counting efficiency of the detectorand A_t – Tracer activity (^{209}Po) added.

The counting background sources of the alpha spectrometer may either to contribute by contamination from possible the used equipment used for the analysis of the sample and alpha particle active materials in their construction material. Therefore, MDA background count rates and counting efficiencies values are parameters in evaluating the measurement results and most importantly othersources of background radiation which must be subtracted from the detector reading[24]&[26]. Considering other parameters detector active area, increase the concentration of the alpha particle active on the plate to be subjected for measurement will help increase the sensitivity. Additionally, the MDA reflects not only the instruments characteristics but takes into consideration some other parameters which influence the measurements like measuring time the amount of the samples used and the chemical yield[27].

3.5.3 Alpha spectrum result interpretation and analysis

The region of interest (ROI) form of analysis was used for Spectral analysis from the measurements made. The ROI is applicable for results interpretation and analysis because it is a simplified situation where only two known peaks are present in the spectrum. Also this is due to the limitation associated with number of the alpha peaks and it energies accompanying it [28].

The following equations were used in the process aimed at calculating the activity concentration of ^{210}Po.

  ➤ Calculation of gross and net count rates from the spectrum

    • Gross count rates for ^{209}Po (G$_{\text{P-209}}$) and ^{210}Po (G$_{\text{P-210}}$)

$$\text{G}_{\text{P-209}} = \frac{n_{209}}{t_c} \qquad\qquad\text{Eqn(10)}$$

$$\text{G}_{\text{P-210}} = \frac{n_{P-210}}{t_C} \qquad\qquad\text{Eqn (11)}$$

- Net count rates

$$N_{P\text{-}209} = G_{P\text{-}209} - G_B \hspace{4cm} \text{Eqn (12)}$$

$$N_{P\text{-}209} = G_{P\text{-}210} - G_B \hspace{4cm} \text{Eqn (13)}$$

➤ Adjustment of tracer (^{209}Po) activity concentration to the count date

$$C_{T,C} = C_{T,T} \times e^{-\lambda_T t_T} \hspace{4cm} \text{Eqn (14)}$$

Therefore, from activity of tracer added when adjusted to the count date is given by

$$A_{T,C} = m_T \times C_{T,C} \hspace{4cm} \text{Eqn (15)}$$

➤ Activity concentration of in sample

$$C_{P,s} = \frac{N_{P-210}}{N_{P-209}} \times \frac{A_{T,C}}{m_s} \hspace{3cm} \text{Eqn (16)}$$

Also $C_{P,S} = \dfrac{C_{P,C}}{e^{-\lambda_P t_S}}$ \hspace{4cm} Eqn (17)

t_T - Number of days from calibration date to count date

t_S - Number of days from separation date to count date

λ_P - decay probability constant for ^{210}Po, λ_T - decay probability constant for ^{209}Po

G_B –Background, $n_{P\text{-}209}$ - Counts ^{209}Po region

m_s – mass of the sample

$N_{P\text{-}210}$- Counts ^{210}Po region, C_{TT} - Tracer activity concentration on the of preparation

$G_{P\text{-}210}$ - Gross count rates for ^{210}Po and $G_{P\text{-}209}$ -Gross count rates for ^{209}Po.

3.5.4 Radiochemical Yield

The suitability of the analytical procedure is evaluated by radiochemical separation. Since the chemical yield for the analyte in sample may be less than 100% due to some possible losses from the sample preparation and measurement stages of this analysis. The radiochemical tracer used for this procedure was polonium-209 which has similar properties to that of polonium-210. The tracer is a certified standard solution was obtained from Oak Ridge National Laboratory (USA) with initial activity of 1.0 µCi (For the procedure, dilution was prepared).

. The radiochemical yield from the is obtain from the spectrum measurement as

$$\eta = \frac{(R_{GT} - R_{BT})}{(\varepsilon C_T m_T)} \hspace{4cm} \text{Eqn (18)}$$

ε is evaluated from the equation below;

$$\varepsilon = \frac{(R_{GPS} - R_{BPS})}{A_{A,PS} * P} \qquad \qquad \text{Eqn (19)}$$

Where

ε is detection efficiency for the alpha particles

η is radiochemical yield of the tracer, ^{210}Po, R_{GT} is gross counting rate of tracer

R_{BT} is blank counting rate of tracer, m_T is mass of tracer used, in g,

R_{BA} is the blank counting rate of the sample, ^{210}Po, R_{GPS} is gross counting rate,

R_{BPS} is background , and $A_{A,PS}$ is activity,

P is probability of each radionuclide in mixed radionuclide point source.

3.6 Uncertainty estimation and validation for the procedure

The main contributing component associated with the procedure to obtain combined uncertainty includes mass of the sample and tracer measured, counts rates of the sample, tracer activity. The classification of these sources of uncertainty were obtained from Type A and Types B components, where Type A is from statistical data from the results of measurements made while Type B is from uncertainties associated from experimental results such manufacturer's specification or from calibration or certified certificate. It is estimate uncertainties associated with the analytical procedure , as it is requirement (ISO/IEC 17025) that laboratories have their measurement results have it uncertainty component attached[28]. The uncertainty budget was evaluated to determine the various uncertainty sources considered in this procedure

3.6.1 Sample preparation Uncertainty sources

Uncertainty sources spanning from sample preparation stage through auto- deposition to alpha spectrometry measurement could be identified. The various uncertainty sources contributions are then quantified with reference to the concentration of the analyte of interest- radionuclide ^{210}Po. The main uncertainty assessment for this analytical procedure includes:

3.6.1.1 Uncertainty associated with sample mass

The estimation of uncertainty associated with sample and tracer masses were evaluated based on the equation from the analytical balance used. With dilution uncertainty for the tracer was estimated by taking into consideration uncertainties due uncertainty information from the flask calibration certificate supplied, repeatability and ambient temperature uncertaintybased on EURACHEM Guide [29].

3.6.1.2 Alpha spectrometric Uncertainty sources

The next after the sample preparation, is the alpha spectrometric measurement and data analysis. The uncertainty components which are the focus for this procedure include counting rates measurement, decay correction factors and other sources of uncertainty linked to the measurement process.

3.6.1.3 Counting rate uncertainty

The spectrum of analyte (^{210}Po) and the tracer (^{209}Po) had relatively better peak resolution, ensuing that the challenge of peak overlapping had no impact on the measurement. The gross counting rates for the analyte and tracer uncertainty were evaluated based on Kanisch (2004, alpha-spectrometric analysis of environmental samples) [30]. In determination of the counting rate uncertainty was carried out using the unlisted equations;

$$u(R_{GT}) = \sqrt{\frac{R_{GT}}{t_G}} \qquad\qquad \text{Eqn (20)}$$

$$u(R_{GA}) = \sqrt{\frac{R_{GA}}{t_G}} \qquad\qquad \text{Eqn (21)}$$

In ensuring that as much as possible to obtain accurate peak areas and correcting any contamination from the analytical procedure. It is important therefore to subtract the background measured from the total counts from the tracer and analyte radionuclide in the in the region of interest (ROI).

$$u(R_T) = \sqrt{\frac{R_{GT}}{t_G} + \frac{R_{Po-209}}{t_B}} \qquad\qquad \text{Eqn (22)}$$

$$u(R_A) = \sqrt{\frac{R_{GA}}{T_G} + \frac{R_{Po-210}}{t_B}}$$ Eqn (23)

Where

R_{GA} – uncertainty of gross counting rate for the analyte, Po-210

R_{GT} - uncertainty of gross counting rate for the tracer, Po-209.

T_B is the acquisition live time for the background

3.6.1.4 Decay correction factors and other uncertainty sources

The uncertainty components associated with decay correction factors were examined to know its uncertainty contribution from the combined standard uncertainty. Isotopic impurities uncertainty for the analyte and tracer were not evaluated and taken into consideration since it uncertainty was considered negligible. The correction factors f_1, f_2, f_3 and f_4 are calculated with theses equations;

$$u(f_1) = f_1(t_s - t_E)U(\lambda_A)$$ Eqn (24)

$$U(f_2) = f_2(\exp(-\lambda_A t_G))\frac{U(\lambda_A)}{\lambda_A}$$ Eqn (25)

$$U(f_3) = f_3(t_s - t_c)U(\lambda_T)$$ Eqn (26)

$$U(f_4) = f_4(1 - f_4\exp(-\lambda_T t_G))\frac{U\lambda_T}{\lambda_T}$$ Eqn (27)

3.6.1.5 The radiochemical yield uncertainty

One vital uncertainty source that is considered for the alpha spectrometry measurement of the sample and the tracer is the radiochemical yield. This uncertainty contribution is included to the total uncertainty budget; tracer is added to the sample because the analyte which is ^{210}Po has share some features with the tracer used where the radiochemical yield evaluated by a counting process using the tracer [28]. The radiochemical yield of the tracer is vital indicator of the performance of the analytical procedure.

Uncertaintyevaluation is connected with the net count of the tracer, the counting efficiency, and the emission rate of the tracer material. The combined standard uncertainty of the radionuclide concentration for ^{210}Po ($a_{A-210Po}$)

$$U(a_{A-210\,Po}) = a_{A-210\,Po} \left\{ \left(\frac{U(A_{210\,Po})}{A_{210\,Po}} \right)^2 + \left(\frac{(m_s)}{m_s} \right)^2 + \left(\frac{U(f_1)}{f_1} \right)^2 + \left(\frac{U(f_2)}{f_2} \right)^2 + \left(\frac{U(f_3)}{f_3} \right)^2 + \right.$$

$$\left. \left(\frac{U(f_4)}{f_4} \right)^2 \right\}^{1/2} \hspace{3cm} \text{Eqn (28)}$$

The accuracy and ensuring that the procedure is fit for purpose is important for routine laboratory analysis. Below gives description of how the samples were treated to determine the parameters needed for validating the analytical procedure.

3.6.2 Validation parameters for the procedure

These parameters were used to evaluate the measured results from the analytical procedure with the reference values. For the purpose of this thesis, the validation parameters and tools selected were based on commonly used by IAEA in validating alpha spectrometry measurement procedure [31]

❖ Radiochemical Yield.
A certified radiochemical tracer, polonium-209 was measured and added to the sample and then was taken through the same process for determining the analyte. The amount of tracer measured was carefully considered with relation to the average activity concentration of polonium in the sample.

❖ Trueness
The reference materials used were spiked with a tracer to evaluate the trueness of the procedure. The best estimate of the true value was obtained from the consensus value from the proficiency test.

❖ Accuracy
The accuracy for this procedure were determined using En-value and z-score.

4. MEASUREMENT, RESULT AND DISCUSSION

4.1 Measurement

Certified reference materials (CRM) from IAEA, which have similar matrices as that of environmental and fly ash samples, were used for this analytical procedure and validation. These CRM were subdivided into parallel samples. The results from each replicate sample were compared to the reference value. Also validation parameters such as recovery, relative bias, z-score, trueness and other important ones were analyzed. Each reference material was subjected to the same analytical procedure to determine the ^{210}Po activity concentration. The reference materials were:

➢ Reference material RGU-1 with certificate IAEA/RL/148 which was prepared by the Canada Centre for Mineral and Energy Technology for IAEA

➢ Soil reference material IAEA from China, which had been spiked with gamma emitting radionuclides.

Soil reference material - obtained from worldwide proficiency test, IAEATEL2012/03. Since these reference materials and certificates used for this procedure came from IAEA, then the results are traceable to IAEA.

4.2 RESULTS

The final data for evaluating the results were obtained usingthe spectra generated from the measurement with the alpha spectrometer. These were then taken through a series of calculations with it associated parameters such as the mass, amount of tracer used, decay correction, uncertainty estimation and others in achieving the final results required.

The results from the analytical process are provided in the tables below gives the activity concentration of the various sample types and its replicates that were used for this procedure. The prepared samplesdeposited on the copper disc were measured at two different distance levels between the detector and where the disc is placed inside the vacuumchamber.

4.2.1 Comparing measured results with reference value

Generally, from the measurement results obtained from the reference materials used for the analysis fall within the acceptable range when comparing it to the reference value. Replicate samples of 3 to 5 were prepared from each reference material.

Figure 5 is the graphical representation of the activity concentration for a certified reference material (certified reference number IAEA444) measured at two different levels (distance between fixed detector and the movable sample stand). R1, R2 and R3 represents the replicate name and L3 and L5 also indicate the level within the vacuum chamber. L3 and L5 mean that the measurements were conducted at a distance of 4 mm and 6 mm (difference between the distance of the detector and the movable sample stand) respectively.

The meaning for L3 and L5 applies to all the figures and tables in this thesis.
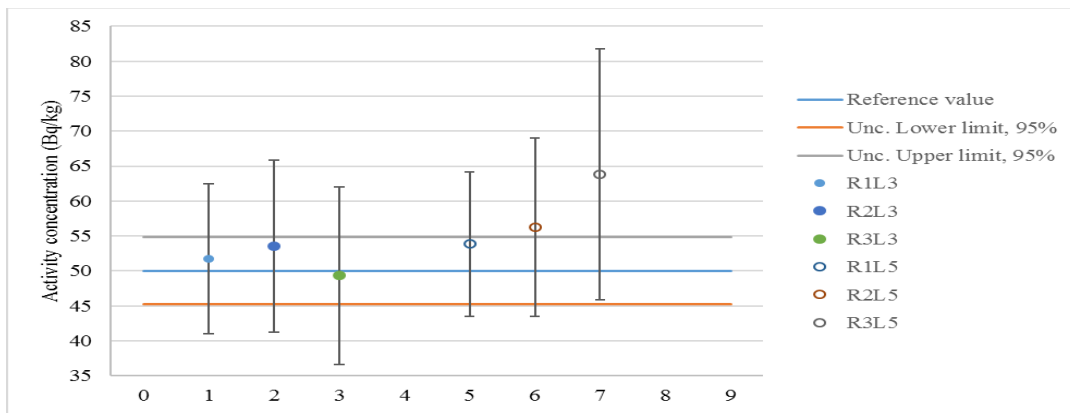
Figure 6: Measured activity concentrationscompared to the reference value (IAEA-444)

The first three values represent measurement results done at L3.The results are nicely distributed within the uncertainty limit of the reference value - two samples (R1L3 and R2L3) are located at upper limit and R3L3 just below the reference value. The mean of measured results for R1L3, R2L3 and R3L3 is (51.54 ± 15.47) Bq/kg, k =2 with a standard deviation of 2.12 (Bq/kg)compared to the reference value (50.0 ± 4.8) Bq/kg, k=2 (all at 95% confidence level). Based on the closeness of the measured value to the reference value these results can be trusted.

Measurement results from L5 had some of the individual results (R2L5 and R3L5) falling outside the uncertainty limits compared to the reference value and the only R1L5 within the upper limit of the reference value. The mean value is (54.82 ±19.69) Bq/kg, k=2 at 95% confidence level with a standard deviation of 7.63(Bq/kg). Although the reference value in this case is found within the range of uncertainty for the measured results, it cannot be fully depended on.

Figure 6 demonstrates the activity concentration and the distribution pattern of the certified reference material (IAEATEL2012/03,) measured at two different levels. R1, R2 and R3 represents the replicate name and the meaning for L3 and L5 remains the same as stated above.
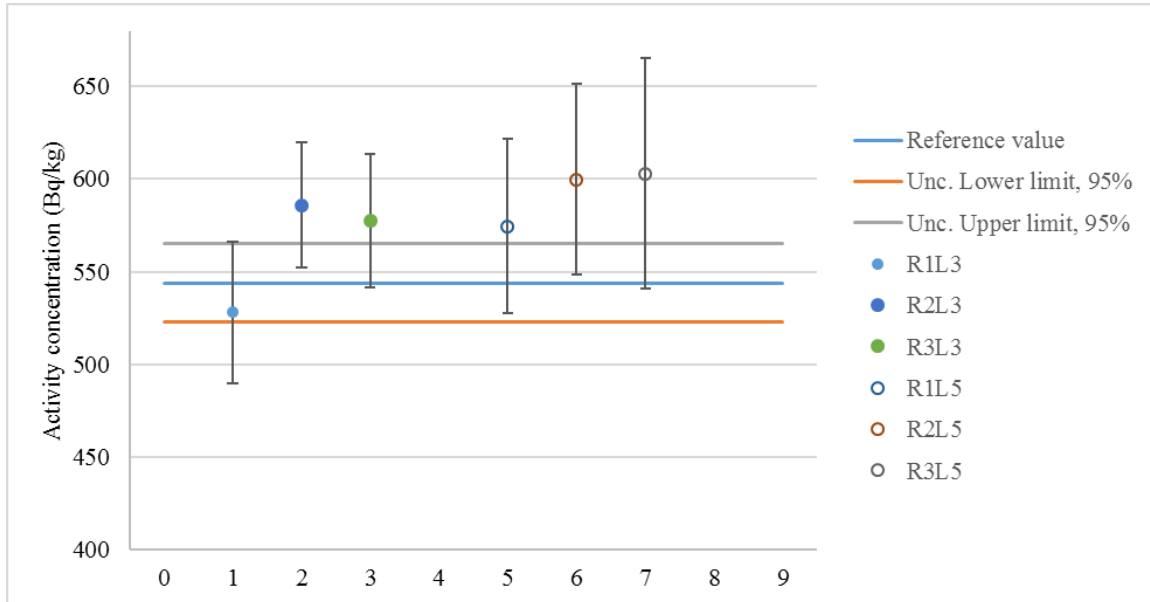
Figure 7: Measured activity concentrations compared to the reference value (IAEATEL2012/03)

The measurement results made at L3 show how the measured results are spread around the reference value and the uncertainty limits. The distribution pattern shows two replicate samples (R2L3 and R3L3) were slightly above the upper limit, but within the uncertainty. Only R1L3 is close to the lower limit of the reference value. The average of the measured results for R2L3, R2L3 and R3L3 is (563.99 ±28) Bq/kg, k =2 with standard deviation of 31.04 (Bq/kg) compared to the reference value (544.0 ± 21.4) Bq/kg, k=2 all at 95% confidence level. It is not excellent when compared to the reference value, but acceptable in the range of uncertainties.

Measurement results for L5 had all the individual results(R1L5, R2L5 and R3L5) falling outside the uncertainty limits compared to the reference value Only found close the upper limit of the reference value. The mean value is (592 ±51) Bq/kg, k=2 at 95% confidence level with a standard deviation of 15.65 (Bq/kg). Although the reference value in this

case is found within the range of uncertainty for the measured results, it cannot be fully depended on.

Figure 7 is the graphical representation for the activity concentration for certified reference material (RGU1) measured at two different levels (L3 and L5).
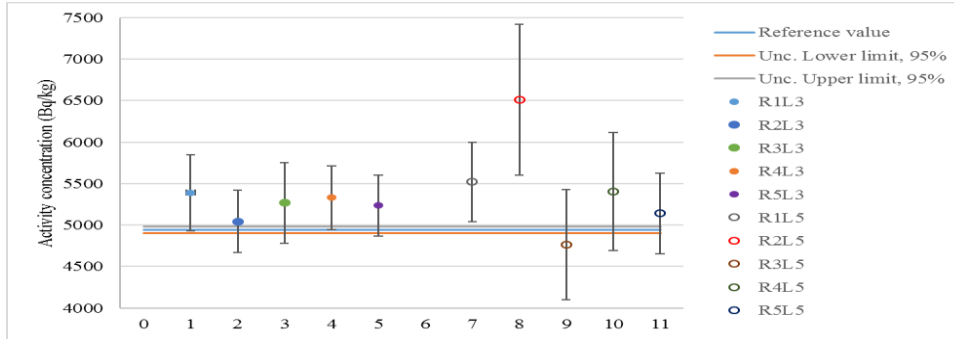
Figure 8: Measured activity concentrations compared to the reference value (IAEA RGU-1).

The measurement results made at L3 show how the measured results are spread around the reference value and it uncertainty limits. The average of this measured results is(5253.99 ± 179.23) Bq/kg, k =2 with standard deviation of 131.74 (Bq/kg) compared to the reference value (4939 ± 39) Bq/kg, k=2 all at 95% confidence level.

RGU-1, measurement results obtained from L5 had some individual results falling outside the uncertainty limits compared to the reference value. The mean value is (5408 ± 168.9) Bq/kg, k=2 at 95% confidence level with a standard deviation of 499.65(Bq/kg). Considering the deviation of the measured value from the reference value although some of the results in this case are found within the range of uncertainty for the measured results, For that reason measured results for L3 could be accepted and that of L5 rejected.

Observation made based on the interpretation of the measured results to reference value:

❖ Measured results obtained from L3 with all the samples demonstrated good very good results, making it more reliable. For L5 not very accurate results were obtained according to the sample reference value compared with.

❖ L3 had the best of results with the reference material with the lowest activity concentration (certified reference number IAEA444). Sample with very high activity

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concentrations had some of the replicate results deviating totally from the reference values and its uncertainty limits

L3 gave a better result - because it was closer to the detector, with high detection efficiency and better spectral data for analysis.

Measurements done at a distance of 4 mm have better results compared to 6 mm. Therefore, with this procedure, to achieve good results, it will be better to have a smaller distance between the source copper and the detector.

Table 1 shows all three sets of certified reference materials and the radiochemical yield or recovery results. The recovery values are good, ranging from 68% and 95%.

Radiochemical yield (%)					
Sample	R1	R2	R3	R4	R5
RM1	77.80	95.00	77.25		
RM2	82.30	75.88	68.10		
RGU1	80.90	93.77	89.80	77.05	74.18

Table 1: Radiochemical yield (%) of the reference materials

4.2.2 Minimum detectable activity (MDA)

Table 2 provides the various MDA's for the samples. It is important to know the MDA because it helps evaluate the possibility of conducting measurements with samples that have low activity concentrations.

Minimum detectable activity , MDA (mBq)										
	R1		R2		R3		R4		R5	
Sample	Value	uncertainty	Value	uncertainty	Value	uncertainty	Value	uncertainty	Value	uncertainty
RM1	1.51	0.0007	1.23	0.001	1.51	0.00084				
RM2	1.73	0.0004	3.89	0.002	2.04	0.00056				
RGU1	11.02	0.005	12.20	0.005	12.73	0.0061	11.56	0.006	12.004	0.007

Table 2 MDA for the various reference materials

The MDA's for two reference materials used provides almost an even and common value throughout. RM1 gives an average value of mBq and RM2 ranges from1.0 to 4 mBq and RGU1 12.5 mBq. The variation of the MDA was based on the counting time used for each sample. RGU-1 had a short counting time because of it high activity concentration compared to RM1 and RM2. The consistency in the MDA value is very important particularly when handling very low level of radioactivity in the environmental samples. This gives a good indication to decision making whether the measured radioactivity concentration is detected from either background, or a real radioactivity level[27].

4.2.3 Tracer recovery

Table 3 shows the recovery of tracer (^{209}Po). The tracer was treated the same way as that of that of the sample from which the analyte is found. It was therefore taken through the analytical procedure measurements starting from sample preparation through to auto-deposition to the alpha spectrometric measurement.

Tracer recovery (%)									
	R1		R2		R3		R4		R5	
Sample	Value	uncertain	Value	uncertainty	Value	uncertainty	Value	uncertainty	Value	uncertainty
RM1	78.65	0.035	96.29	0.039	78.59	0.044				
RM2	82.47	0.020	68.29	0.031	76.04	0.021				
RGU1	81.31	0.038	94.22	0.042	90.26	0.041	77.51	0.041	74.62	0.04

Table 3: Tracer recovery

The tracer recovery added to the sample gives a very good indication of the efficiency of this analytical process. This provides a reason to make this results from the procedure to be reliable and helps know the percentage recovery that is expected from the analysis. With recovery percentage range between 74 to 96 makes the analytical procedure fit for purpose.

4.3 Uncertainty contributions.

The main uncertainty sources that were evaluated for this procedure in order to obtain the combined uncertainty were, mass of the sample and tracer, count rates of the sample and tracer, tracer activity and chemical recovery. Figures 9 and 10 shows the uncertainty sources contributions in terms of percentage. Additionally, appendices ……….
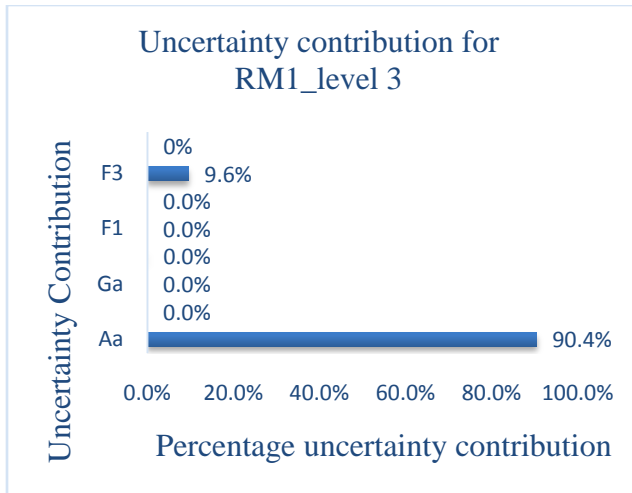
Figure 9: Uncertainty contribution for RM1_Level 3
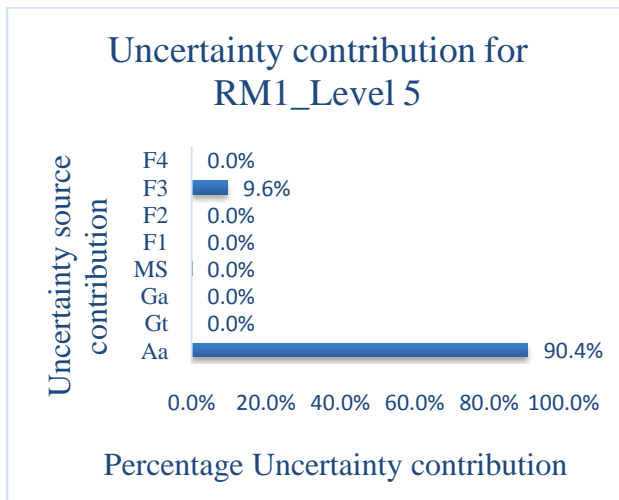
Figure 10: Uncertainty distribution for RM1 at level 5

➤ Activity of the analyte A_a, on the electroplated copper disk recorded the highest uncertainty contribution. This is followed by f_3– correction for decay of ^{209}Po from its calibration date to measurement.

➤ Uncertainty sources that could be neglected include;

- Gross count rates for ^{209}Po (G_{P-209}) and ^{210}Po (G_{P-210})
- f_2 – correction for decay of ^{210}Po during the interval period t_G
- f_3– correction for decay of ^{209}Po from its calibration date to measurement
- ms is the mass of the sample

4.4 Validation parameters used

Since this thesis work is aim at finding a suitable measurement procedure for measuring polonium-210, the discussion of the result will focus comparing the results from the analytical procedure used in the laboratory with the started reference values on the various validation parameters that will make this procedure fit purpose. Below provide the parameters used for this analysis.

4.4.1 Trueness

This is evaluated using

$$A_1 = \left| C_{exp} - C_{exp} \right| \qquad\qquad \text{Eqn (29)}$$

$$A_2 = \sqrt{u^2_{meas} + u^2_{ref}} \qquad\qquad \text{Eqn (30)}$$

If $A_1 < A_2$

By the proficiency testing system used by IAEA Terrestrial Environment laboratory take the trueness of the reported results. The results is considered acceptable if $A_1 < A_2$[31]

Table 3 and 4 are used to demonstrate the trueness of the measured results based on Eqn (29) & (30).

Distance between the detector and analyte on the disc, level 3							
Proficiency test sample	Sample name	analyte	Reference value [Bq/ Kg]	Measured value [Bq/Kg]	A1	A2	Final score rating
Certified reference material , RM 1 (IAEA444)	R1	Po-210	50	51.74	1.74	30.27	$\mathcal{A}$
	R2	Po-210	50	53.56	3.56	33.97	$\mathcal{A}$
	R3	Po-210	50	49.32	0.68	34.94	$\mathcal{A}$
Certified reference material ,RM 2 (IAEATEL201203)	R1	Po-210	544	318.53	225.47	87.35	$\mathcal{F}$
	R2	Po-210	544	528.49	15.51	113.38	$\mathcal{A}$
	R3	Po-210	544	586.03	42.03	102.70	$\mathcal{A}$
	R4	Po-210	544	577.46	33.46	107.82	$\mathcal{A}$
Reference material RGU-1 (IAEA/RL/148)	R1	Po-210	4939	5390.76	451.76	1190.38	$\mathcal{A}$
	R2	Po-210	4939	5043.02	104.02	972.87	$\mathcal{A}$
	R4	Po-210	4939	5329.42	390.42	991.84	$\mathcal{A}$
	R5	Po-210	4939	5235.31	296.31	948.82	$\mathcal{A}$

Table 4: En-value and z-score

Distance between the detector and analyte on the disc, level 5							
Proficiency test sample	Sample name	analyte	Reference value [Bq/Kg]	Measured value [Bq/Kg]	A1	A2	Final score
Certified reference material , RM 1 (IAEA444)	R1	Po-210	50	53.85	3.85	29.32	A
	R2	Po-210	50	56.29	6.29	35.20	A
	R3	Po-210	50	45.29	4.71	40.50	A
	R4	Po-210	50	63.83	13.83	47.99	A
Certified reference material ,RM 2 (IAEATEL201203)	R1	Po-210	544	574.53	30.53	133.50	A
	R2	Po-210	544	599.88	55.88	169.51	A
	R3	Po-210	544	603.18	59.18	143.40	A
Reference material RGU-1 (IAEA/RL/148)	R1	Po-210	4939	5520.67	581.67	1234.12	A
	R2	Po-210	4939	6510.86	1571.86	2341.04	A
	R4	Po-210	4939	6026.87	1087.87	2999.59	A
	R5	Po-210	4939	5140.62	201.62	1250.13	A

Table 5: Trueness evaluation at level 5

Base on the evaluation condition stated above, all the measured results from this procedure that had it value very close to the reference value or falls within the uncertainty range of the reference value had a positive mark (A). This therefore gives an indication that in terms of trueness using the formula above (equ.) the procedure is fit for purpose

4.4.2 Accuracy

In evaluating the compatibility of the results,the z-score and E_n-value between measured values and certified reference values. A 95% confidence level for uncertainty estimation was used to determine En-value.

➢ Z-score is given by:

$$z = \frac{x_{lab} - x_{ref}}{\sigma}$$ Eqn (31)

Where, x_{lab} = Laboratory result, x_{ref} = reference value

σ = Standarddeviation of laboratory results

Interpretation of z-score

Value range	Interpretation
z<2	measurement is satisfactory
2<z<3	measurement is questionable
z>3	measurement is poor thus require further analysis

Table 6: Interpretation of z-score

Secondly, accuracy of the procedure was examined using E_n-value

$$E_n = \frac{\bar{X}_{meas} - u_{ref}}{\sqrt{u^2_{meas} + u^2_{ref}}}$$
Eqn (32)

Where:

u_{ref} = certified value and $\bar{X}_{meas}$ is the mean value obtained from the measurement

u_{meas} and u_{ref} is expanded uncertainty of certified value and laboratory value respectively.

Interpretation of En values:

| En | ≤ 1: indicate that an experimental value is consistent with reference value.

| En | > 1: indicate that an experimental value is NOT consistent with reference value.

Tables 6 and 7 provides the accuracy determination using En-value and z-score.

Distance between the detector and analyte on the disc, level 3						
Proficiency test sample	Sample name	analyte	Reference value [Bq/Kg]	Measured value [Bq/Kg]	En-value	z-score
Certified reference material , RM 1 (IAEA444)	R1	Po-210	50	51.74	0.15	0.35
	R2	Po-210	50	53.56	0.27	0.71
	R3	Po-210	50	49.32	-0.05	-0.14
Certified reference material ,RM 2 (IAEATEL201203)	R1	Po-210	544	318.53	-6.66	-4.14
	R2	Po-210	544	528.49	-0.35	-0.29
	R3	Po-210	544	586.03	1.06	0.77
	R4	Po-210	544	577.46	0.80	0.62
Reference material RGU-1 (IAEA/RL/148)	R1	Po-210	4939	5390.76	0.98	0.91
	R2	Po-210	4939	5043.02	0.28	0.21
	R3	Po-210	4939	5267.19	0.67	0.66
	R4	Po-210	4939	5329.42	1.02	0.79
	R5	Po-210	4939	5235.31	**0.81**	**0.60**

Table 7: En-value and z-score

Distance between the detector and analyte on the disc, level 5						
Proficiency test sample	Sample name	analyte	Reference value [Bq/ Kg]	Measured value [Bq/Kg]	En-value	z-score
Certified reference material , RM 1 (IAEA444)	R1	Po-210	50	53.8514	0.34	0.77
	R2	Po-210	50	56.2922	0.46	1.26
	R3	Po-210	50	45.2921	-0.30	-0.94
	R4	Po-210	50	63.8262	0.74	2.77
Certified reference material ,RM 2 (IAEATEL201203)	R1	Po-210	544	574.5302	0.59	0.56
	R2	Po-210	544	599.8790	0.85	1.03
	R3	Po-210	544	603.1767	1.06	1.09
Reference material RGU-1 (IAEA/RL/148)	R1	Po-210	4939	5520.6717	1.22	1.18
	R2	Po-210	4939	6510.8602	1.73	3.18
	R3	Po-210	4939	2289.9351	-18.30	-5.36
	R4	Po-210	4939	6026.8656	0.94	2.20
	R5	Po-210	4939	5140.6237	0.42	0.41

Table 8: En-value and z-score at level 5

From the tables above the En-value and the zero was used also as a source of comparison between the reference value and that of the reference value. Although not all the measured results fell within the accepted range. Majority pass the test. The following observation and interpretation could be made from the two tables (6&7).

❖ According to the scoring format for both En-value and z-score, measuring from L3, RM1passed both and as well as for L5 expect that R4 from table 7 had a value (2.77) which is very close to the upper limit for z-score.

❖ RM2 relatively had a better accuracy scoring particularly with measurements done at L3 where only one replicate sample failed the En-value slightly with a value of 1.06. This also applies to RGU1 replicate samples which much better results at L3 than that of L5.

5. CONCLUSION

Theaim of the thesis was to develop a suitablemeasurement procedure and validating it to be applicable for measuring polonium-210 in environmental samples using alpha spectroscopy. The mainemphasis was on the sample preparation stage, determining activity concentration of the samplesand selecting suitable validationparameters. The validation parameters used for this procedure are: tracer recovery, trueness, accuracy (En-value, z-score) and relative bias.

The **sample preparation**; included using a suitable microwave digestion programmeand amount of reagents as well as suitable deposition parameters. Based on literature review and experimental results The final results from the analytical procedure demonstrated that the chosen approach is well applicable and could be used for environmental samples that have similar matrix.

The alpha spectrometry measurements were done at two different levels; that is the distance between the detector and the sample source, revealed that the level closer to the detector gave very good results compared to the lower level. One reason was to ensure that the spectrum for the tracer and that of analyte do not have too much tailing to cause overlapping of peaks.

validating the procedure was carried out in accordance with IAEA and similar analytical research publications in this field. All the samples which had the measuredvalue close to the reference value or fells within the uncertainty limit,passed the validation parameters test, whereas the results found outside the value and uncertainty limits of the reference value could not be fully validated by all the validation parameters.

Additionally, sources of uncertainty contributions were established to be in conformity with IAEA alpha spectroscopic measurements and with cited publications dedicated to uncertainty determination for environmental samplesusing alpha spectrometric measurements. The greatest source of uncertainty came from the sample measurement statistics.

Based on the above reasons, this procedure can provide true and reliable results, and therefore procedure is fit for its intended purpose.

Since this measurement procedure is to be adopted and used in the laboratory, the following recommendations will be made:

1. Care must be taken during the evaporation to dryness stage not to inflict losses due to the volatile nature of the analyte (^{210}Po)

2. It is important to prepare replicate(minimum ofthree) of the analyzed sample to guarantee the trueness or the accuracy of the results. This helps to save time since the preparation part for this procedure time consuming.

3. Suitable distance between the detector and the sample source should be selected. This was evident in the procedure where the same sample source was measured at two different levels. Results demonstrated clear difference in deviations from the expected value between the two groups showing the importance of selecting the right level.

4. The time duration between the sample digestion and deposition onto the disc (copper or silver) should be short as possible. This is due to the possibility of additional ^{210}Po ingrowth from ^{210}Pb during this period and this may cause systematically higher results. This may cause a shift in the expected ratio between the analyte and the tracer.

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7. APPENDICES

Appendix I Equipment's and supplies used

- ✓ Alpha Spectrometry System.
  - Canberra Alpha detector system (Model 7401).
  - Ultra- Ion-Implanted-Silicon Charged-Particle detector,
  - Vacuum pump and vacuum chamber.

- ✓ Planchets
  - Copper disc; thickness 0.2 mm, purity 99.9%
- ✓ Hot Plate with magnetic stirrer
- ✓ Glass Beakers.
- ✓ Fume Hood.
- ✓ Teflon Beakers.
- ✓ Stirring Bar.
- ✓ Wash Bottles.
- ✓ Graduated Cylinder.
- ✓ Volumetric Flasks.
- ✓ Pipette
- ✓ Weighing (Precision balance)
- ✓ Drying oven
- ✓ Disposable pipettes
- ✓ Thermometer
- ✓ Teflon holder
- ✓ Centrifugation equipment

Appendix II Uncertainty source contribution table for the reference materials.

	A_a	G_t	G_a	M_S	F_1	F_2	F_3	F_4
	0.02883978	0.025579	0.025579	0.025579	0.025579	0.025579	0.0255785	0.02558
	0.00782794	0.01	0.01	0.007828	0.007828	0.007828	0.0078279	0.00783
	0.00484954	0.00485	0.00526	0.00485	0.00485	0.00485	0.0048495	0.00485
	0.50213333	0.502133	0.502133	0.503073	0.502133	0.502133	0.5021333	0.50213
	1.16996574	1.169966	1.169966	1.169966	1.169966	1.169966	1.1699657	1.16997
	1.00250669	1.002507	1.002507	1.002507	1.002507	1.002508	1.0025067	1.00251
	0.96563901	0.965639	0.965639	0.965639	0.965639	0.965639	1.0057243	0.96564
	1.0000093	1.000009	1.000009	1.000009	1.000009	1.000009	1.0000093	1.00002
$C_{RM1\_L3\_sample}$	65.0507214	57.694678	57.69468	57.58687	57.6947	57.69477	60.089682	57.6953
Delta_C_RM1_L3_sample	7.35604348	0	0	-0.107803	2.26E-05	9.68E-05	2.3950042	0.00065
Delta_C_RM1_L3_sample_Squared	54.1113756	0	0	0.011622	5.1E-10	9.36E-09	5.7360453	4.2E-07
Sum of squares	59.8590429							
Uncertainty contribution	90.4%	0.0%	0.0%	0.0%	0.0%	0.0%	9.6%	0%
Results								
$C_{RM1\_L3\_sample}$ = (	57.695	±	15.474) **Bq/g**		k = 2			

	A_a	G_t	G_a	M_S	F_1	F_2	F_3	F_4
	0.024666356	0.02142979	0.02142979	0.02142979	0.02142979	0.0214298	0.02142979	0.02143
	0.005308003	0.01	0.01	0.005308	0.005308	0.005308	0.005308	0.005308
	0.003195776	0.00319578	0.00360773	0.00319578	0.00319578	0.0031958	0.00319578	0.003196
	0.5018	0.5018	0.5018	0.50274	0.5018	0.5018	0.5018	0.5018
	1.49960743	1.49960743	1.49960743	1.49960743	1.49960922	1.4996074	1.49960743	1.499607
	1.002274219	1.00227422	1.00227422	1.00227422	1.00227422	1.002276	1.00227422	1.002274
	0.965418858	0.96541886	0.96541886	0.96541886	0.96541886	0.9654189	1.01289809	0.965419
	1.000008441	1.00000844	1.00000844	1.00000844	1.00000844	1.0000084	1.00000844	1.00002
$C_{RM1\_L5\_sample}$	71.32765235	61.968482	61.9684818	61.852616	61.968556	61.968592	65.0160874	61.96922
Delta_C_RM1_L5_sample	9.359170516	0	0	-0.1158658	7.4179E-05	0.0001106	3.0476056	0.000742
Delta_C_RM1_L5_sample_Squared	87.59407274	0	0	0.01342488	5.5025E-09	1.223E-08	9.2878999	5.51E-07
Sum of squares	96.8953981							
Uncertainty contribution	90.4%	0.0%	0.0%	0.0%	0.0%	0.0%	9.6%	0.0%
Results								
$C_{RM1\_L5\_sample}$ = (	61.968	±	19.687) **Bq/kg**					

	A_a	G_t	G_a	M_S	F_1	F_2	F_3	F_4
	0.172900394	0.17203397	0.17203397	0.17203397	0.17203397	0.172034	0.17203397	0.172034
	0.052107694	0.41	0.05	0.05210769	0.05210769	0.0521077	0.05210769	0.052108
	0.044634163	0.04463416	0.38337779	0.04463416	0.04463416	0.0446342	0.04463416	0.044634
	0.5014	0.5014	0.5014	0.50248542	0.5014	0.5014	0.5014	0.5014
	1.759097932	1.75909793	1.75909793	1.75909793	1.75910189	1.7590979	1.75909793	1.759098
	1.001331323	1.00133132	1.00133132	1.00133132	1.00133132	1.0013324	1.00133132	1.001331
	1.001331323	1.00133132	1.00133132	1.00133132	1.00133132	1.0013313	1.00135641	1.001331
	0.964988522	0.96498852	0.96498852	0.96498852	0.96498852	0.9649885	0.96498852	0.964996
$C_{RM2\_L3\_sample}$	586.9206955	583.97956	583.979557	582.718103	583.98087	583.98017	583.994189	583.9838
Delta_C_RM2_L3_sample	2.941138532	0	0	-1.261454	0.00131256	0.0006147	0.0146324	0.004274
Delta_C_RM2_L3_sample_Squared	8.650295865	0	0	1.59126608	1.7228E-06	3.779E-07	0.00021411	1.83E-05
Sum of squares	10.24179642							
Uncertainty contribution	84.5%	0.0%	0.0%	15.5%	0.0%	0.0%	0.0%	0.0%
Results								
$C_{RM2\_L3\_sample}$ = (	583.980	±	6.401) Bq/g	, k = 2				

	A_a	G_t	G_a	M_S	F_1	F_2	F_3	F_4
	0.213712363	0.21281142	0.21281142	0.21281142	0.21281142	0.2128114	0.21281142	0.21281142
	0.015656256	0.40	0.02	0.01565626	0.01565626	0.0156563	0.01565626	0.01565626
	0.015713245	0.01571324	0.38372831	0.01571324	0.01571324	0.0157132	0.01571324	0.01571324
	0.499733333	0.49973333	0.49973333	0.50067333	0.49973333	0.4997333	0.49973333	0.49973333
	1.670345405	1.6703454	1.6703454	1.6703454	1.67034755	1.6703454	1.6703454	1.6703454
	1.001860249	1.00186025	1.00186025	1.00186025	1.00186025	1.0018616	1.00186025	1.00186025
	0.964990824	0.96499082	0.96499082	0.96499082	0.96499082	0.9649908	0.96501255	0.96499082
	1.000006904	1.0000069	1.0000069	1.0000069	1.0000069	1.0000069	1.0000069	1.00001621
$C_{RM2\_L5\_sample}$	690.6069	687.6956	687.6956	686.4044	687.6964	687.6965	687.7110	687.7020
Delta_C_RM2_L5_sample	2.9114	0.0000	0.0000	-1.2911	0.0009	0.0010	0.0155	0.0064
Delta_C_RM2_L5_sample_Squared	8.4762	0.0000	0.0000	1.6670	0.0000	0.0000	0.0002	0.0000
Sum of squares	10.1435							
Uncertainty contribution	83.6%	0.0%	0.0%	16.4%	0.0%	0.0%	0.0%	0.0%
Results								
$C_{RM2\_L5\_sample}$ = (	687.696	±	6.370) Bq/g	k = 2				

	A_a	G_t	G_a	M_S	F_1	F_2	F_3	F_4
	0.554266257	0.547946385	0.547946385	0.547946385	0.547946385	0.54794638	0.547946385	0.5479464
	0.045221165	0.52	0.05	0.045221165	0.045221165	0.04522116	0.045221165	0.0452212
	0.133260139	0.133260139	0.480895165	0.133260139	0.133260139	0.13326014	0.133260139	0.1332601
	0.1073	0.1073	0.1073	0.108513535	0.1073	0.1073	0.1073	0.1073
	1.079218672	1.079218672	1.079218672	1.079218672	1.079218942	1.07921867	1.079218672	1.0792187
	1.001860249	1.001860249	1.001860249	1.001860249	1.001860249	1.00186059	1.001860249	1.0018602
	0.963665483	0.963665483	0.963665483	0.963665483	0.963665483	0.96366548	0.963693496	0.9636655
	1.000001473	1.000001473	1.000001473	1.000001473	1.000001473	1.00000147	1.000001473	1.0000035
$C_{RGU1\_L3\_sample}$	5382.230054	5320.8606	5320.860624	5261.356071	5320.861955	5320.86246	5321.015296	5320.8714
Delta_C_RGU1_L3_sample	61.36942975	0	0	-59.50455351	0.00133065	0.00183519	0.154671479	0.0107659
Delta_C_RGU1_L3_sample_Squared	3766.206908	0	0	3540.791888	1.77063E-06	3.3679E-06	0.023923266	0.0001159
Sum of squares	7307.02284							
Uncertainty contribution	51.5%	0.0%	0.0%	48.5%	0.0%	0.0%	0.0%	0.0%
Results								
$BC_{RGU1\_L3\_sample}$ = (	5320.861	±		170.962	) Bq/kg			

	A_a	G_t	G_a	M_S	F_1	F_2	F_3	F_4
	0.54931856	0.542808	0.542808	0.542808	0.542808	0.542808	0.5428082	0.54281
	0.0480724	0.64	0.05	0.048072	0.048072	0.048072	0.0480724	0.04807
	0.10363793	0.103638	0.527907	0.103638	0.103638	0.103638	0.1036379	0.10364
	0.1073	0.1073	0.1073	0.108514	0.1073	0.1073	0.1073	0.1073
	1.0555969	1.055597	1.055597	1.055597	1.055597	1.055597	1.0555969	1.0556
	1.00033893	1.000339	1.000339	1.000339	1.000339	1.000339	1.0003389	1.00034
	1.00033893	1.000339	1.000339	1.000339	1.000339	1.000339	1.0003669	1.00034
	0.96374438	0.963744	0.963744	0.963744	0.963744	0.963744	0.9637444	0.96375
$C_{RGU1\_L5\_sample}$	5211.69342	5149.9264	5149.926	5092.333	5149.927	5149.928	5150.0706	5149.94
Delta_C_RGU1_L5_sample	61.7670252	0	0	-57.59295	0.000898	0.001351	0.1442262	0.01051
Delta_C_RGU1_L5_sample_Squared	3815.1654	0	0	3316.948	8.07E-07	1.82E-06	0.0208012	0.00011
Sum of squares	7132.13444							
Uncertainty contribution	53.5%	0.0%	0.0%	46.5%	0.0%	0.0%	0.0%	0.0%
Results								
$C_{RGU1\_L5\_sample}$ = (	5149.926	±		168.904	) Bq/g			

Appendix III graphical representation of uncertainty source contribution for the measurement

Uncertainty contribution for RM2_L3

Uncertainty contribution	percentage of uncertainty contribution
F4	0.0%
F3	3.5%
F2	0.0%
F1	0.0%
MS	0.0%
Ga	0.0%
Gt	0.0%
Aa	96.5%

Uncertainty contribution for RM2_level 5

Uncertainty contribution RGU1_L5
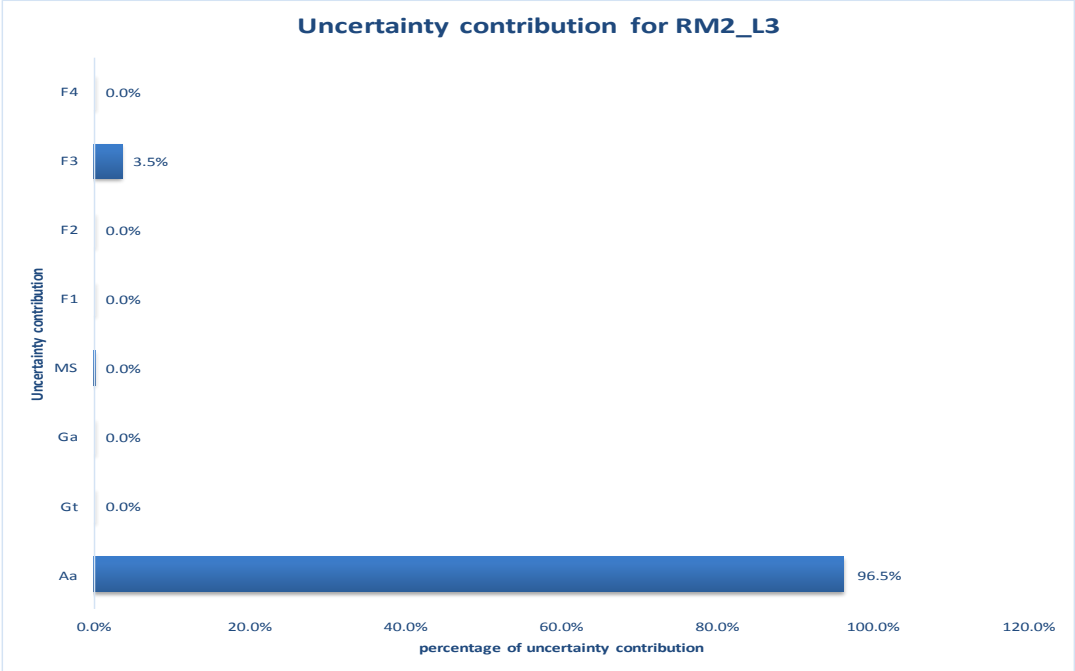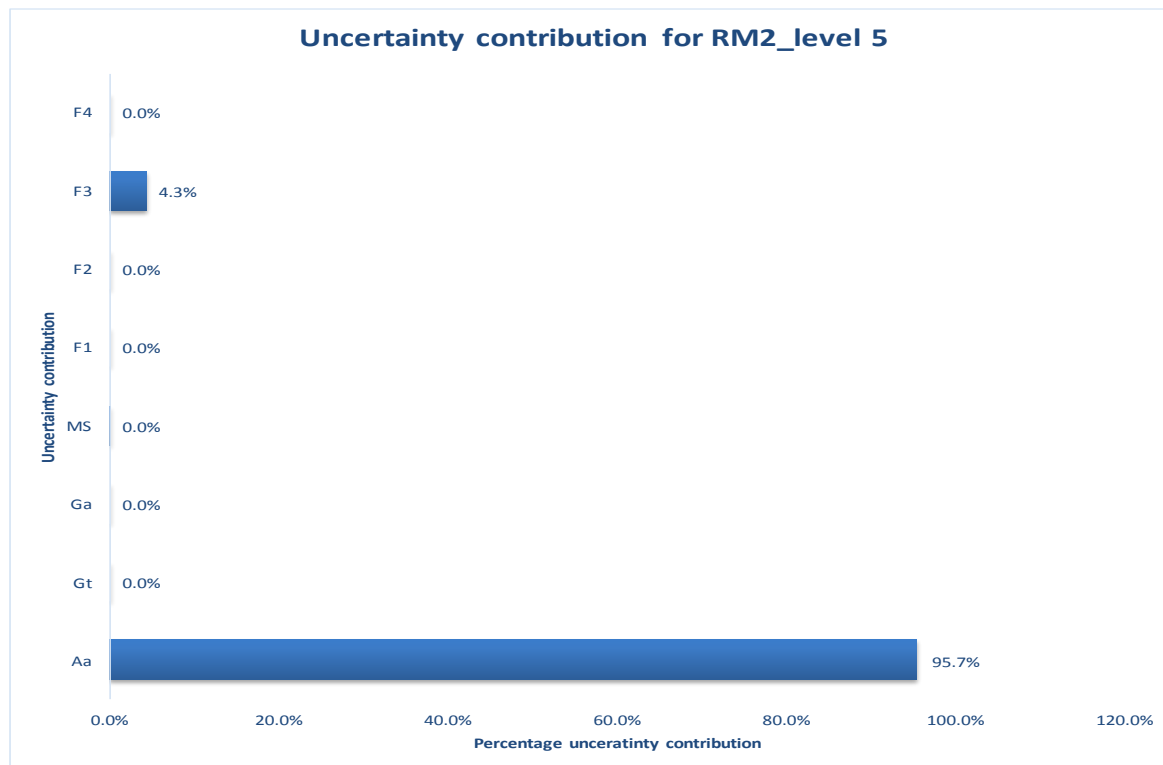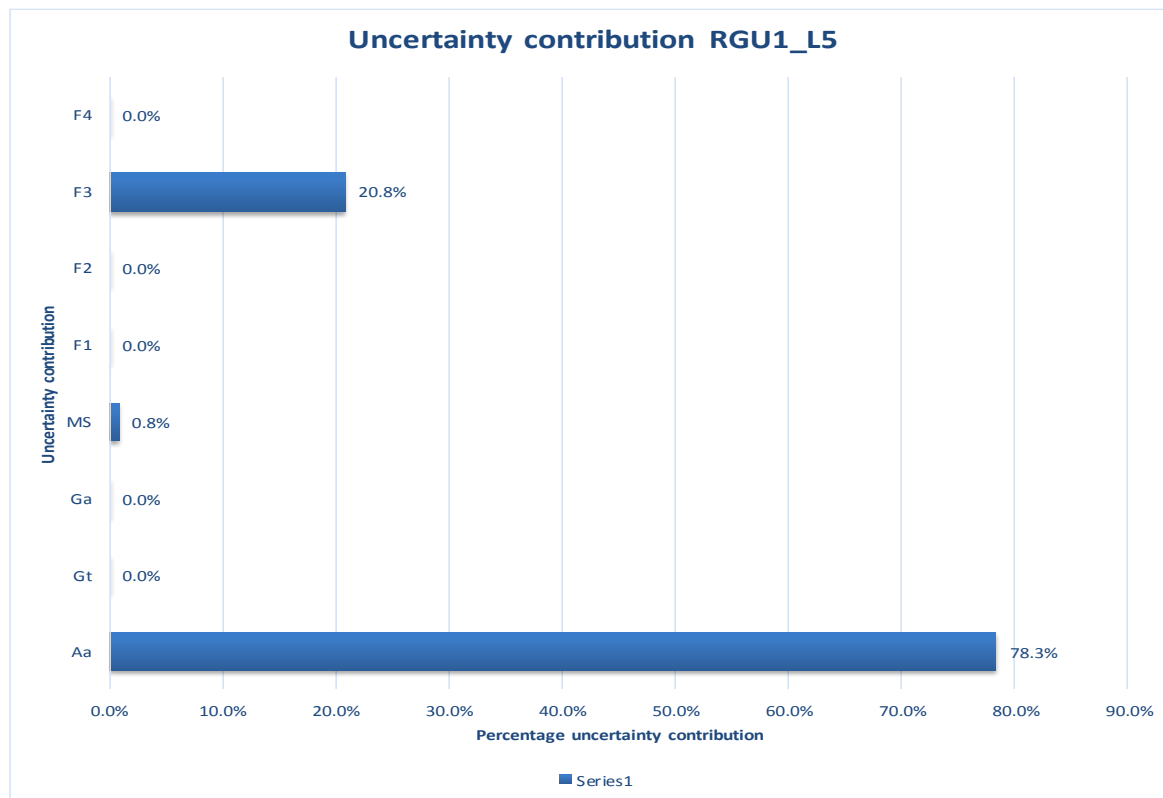
Appendix IV Relative bias for L3 and L5

Distance between the detector and analyte on the disc, level 3					
Proficiency test sample	Sample name	analyte	Reference value [Bq/	Measured value [Bq/Kg]	Relative Bias (%)
Certified reference material , RM 1 (IAEA444)	R1	Po-210	50.00	51.74	3.48
	R2	Po-210	50.00	53.56	7.11
	R3	Po-210	50.00	49.32	-1.35
Certified reference material ,RM 2 (IAEATEL201203)	R1	Po-210	544.00	318.53	-41.45
	R2	Po-210	544.00	528.49	-2.85
	R3	Po-210	544.00	586.03	7.73
	R4	Po-210	544.00	577.46	6.15
Reference material RGU-1 (IAEA/RL/148)	R1R2	Po-210	4939.00	5390.76	9.15
	R2	Po-210	4939.00	5043.02	2.11
	R3	Po-210	4939.00	5267.19	6.64
	R4	Po-210	4939.00	5329.42	7.90
	R5	Po-210	4939.00	5235.31	6.00

Distance between the detector and analyte on the disc, level 5					
Proficiency test sample	Sample name	analyte	Reference value [Bq/ Kg]	Measured value [Bq/Kg]	Relative Bias (%)
Certified reference material , RM 1 (IAEA444)	**R1**	Po-210	50	53.85	7.70
	R2	Po-210	50	56.29	12.58
	R3	Po-210	50	45.29	-9.42
	R4	Po-210	50	63.83	27.65
Certified reference material ,RM 2 (IAEATEL201203)	**R1**	Po-210	544	574.53	5.61
	R2	Po-210	544	599.88	10.27
	R3	Po-210	544	603.18	10.88
Reference material RGU-1 (IAEA/RL/148)	R1	Po-210	4939	5520.67	11.78
	R2	Po-210	4939	6510.86	31.83
	R3	Po-210	4939	2289.94	-53.64
	R4	Po-210	4939	6026.87	22.03
	R5	Po-210	4939	5140.62	4.08

8 KOKKUVÕTE

"Analüütilise mõõteprotseduuri valideerimine poloonium-210 (^{210}Po) tuvastamiseks keskkonnaproovidest alfaspektromeetrilisel meetodil"

Francis Gyakwaa

Käesoleva magistritöö eesmärgiks oli töötada välja ning valideerida mõõteprotseduur poloonium-210 tuvastamiseks keskkonnaproovides rakendades alfaspektromeetrilist mõõtemeetodit. Põhiline rõhk oli suunatud proovide ettevalmistamisele mõõtmiseks, saadud väärtuste spektraalanalüüsile ning oluliste valideerimisparameetrite hindamisele. Valitud parameetrid olid: tõesus, täpsus (E_n – väärtus ja z-väärtus), saagis ja suhteline hälve.

Proovide ettevalmistamise etapp hõlmas sobiva programmi ning kemikaalide leidmist proovide lahustamiseks mikrolaine mineralisaatoriga ning laborioludes rakendatavate sadestamisparameetrite tuvastamist. Valik tehti nii olemasoleva teaduskirjanduse kui ka eksperimentaalselt saadud tulemuste alusel. Vastava analüütilise protseduuri katsetulemused näitasid selle kasutamise sobivust valitud proovide töötlemisel ning analüüsimisel.

Proovide alfaspektromeetrilised mõõtmised viidi läbi kahel tasandil. Saadud tulemuste alusel oli võimalik järeldada, et detektorile lähemal tehtud mõõtmised omasid täpsemat kokkulangevust eeldatavate tulemustega võrreldes mõõtmistega kaugemal tasandil.

Valideerimine viidi läbi vastavalt IAEA ja teiste kättesaadavate ja asjakohaste teaduspublikatsioonide alusel, mis on seotud antud valdkonnaga. Suurem osa tulemusi, mis antud magistritöös saadi, oli võimalik valitud parameetrite alusel valideerida. Erinevate määramatuse komponentide hinnangul selgus, et kõige suurema osa annab statistiline määramatus, mis tuleneb proovi mõõtmisest.

Saadud tulemustest lähtuvalt saab autor teha järgnevad soovitused:

1. Proovide töötlemise käigus tuleb täiendavat tähelepanu pöörata proovide aurutamisele, et vältida polooniumi kadu (tulenevalt elemendi lenduvusest);

2. Oluline on valmistada uuritavast proovist paralleelproove, et tagada tõesed tulemused. Ebakõlade tekkel on kogu mõõteprotseduuri kordamine ajamahukas tegevus, mida võimalusel tuleks vältida.

3. Tuleb valida optimaalne proovi mõõtekaugus detektorist. Saadud tulemused näitasid selgelt erinevust nii tulemuste täpsuses kui ka standardhälvetes, kui proove mõõdeti erinevatel kaugustel.

4. Pärast proovi lahustamist tuleks proov esimesel võimalusel suunata polooniumi sadestamisele. Pikem ajaline viivitus nende kahe etapi vahel vähendab mõõtetäpsust ning suurendab lõpptulemuste määramatust tulenevalt võimalikule nihkele ^{210}Po ja ^{209}Po suhteväärtustes.

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Validation of alpha spectrometric analytical measurement procedure for the determination of Polonium-210 (^{210}Po) in environmental samples

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Information sheet

Title in Estonian

"Analüütilise mõõteprotseduuri valideerimine poloonium-210 (^{210}Po) tuvastamiseks keskkonnaproovidest alfaspektromeetrilisel meetodil"

summary in Estonian

Käesolev magistritöö keskendub sobiva alfaspektromeetrilise mõõteprotseduuri välja töötamisele ning valideerimisele eesmärgiga seda rakendada laboris, kus esineb vajadus rutiinseteks ^{210}Po aktiivsuse kontsentratsioonide tuvastamiseks keskkonnaproovides. Selgitamaks välja protseduuri rakendatavuse ning asjakohasuse hinnati järgnevaid valideerimisparameetreid: tõesus, täpsus (E$_n$ väärtus ja z-väärtus), suhteline hälve ning markeri (^{209}Po) saagis. Samuti hinnati erinevate määramatuste komponentide osakaalu mõõtmistulemustes.

 Keywords in Estonian

Poloonium-210, Valideerimine, Alfa spektromeetria , Looduslik kiirgusallikas

 Title in English

Validation of alpha spectrometric analytical measurement procedure for the determination of Polonium-210 (^{210}Po) in environmental samples

summary in English

The thesis aims at finding suitable alpha spectrometry measurement procedure and validating it to be implemented in the laboratory where it can be used for routine analytical procedure for the determination of ^{210}Po in environmental samples. In establishing if the procedure is fit for the intended purpose, the following validation parameters were determined: trueness, accuracy (En-value, z-score), relative bias, and tracer recovery. Also the main sources of uncertainty and their percentage contributions were established.

Keywords in English: *Polonium-210, validation, alpha spectrometry, natural radiation source*

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