

## ROBUSTNESS OF POLONIUM-210 TEST METHOD IN TERMS OF PHYSICAL AND CHEMICAL ASPECTS

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### ABSTRACT

*Accurate measurement of  $^{210}\text{Po}$  in environmental samples is very important because  $^{210}\text{Po}$  is a major contributor to the natural radiation dose received by all living organisms. This study is carried out since no comprehensive work validates the  $^{210}\text{Po}$  in-house test method in Radiochemistry and Environmental Group, Malaysian Nuclear Agency. This paper defines the procedure used to determine  $^{210}\text{Po}$  in sediment samples, which involved acid digestion followed by auto-plating for counting using an alpha spectrometry system. Validation in terms of robustness including physical and chemical aspects was done. The physical parameter involves different counting geometry, plating time, and counting time intervals, while chemical aspects include iron content in the sample. This study found that this method is robust.*

**Keywords/Kata kunci:** Polonium-210, alpha spectrometry, method validation, robustness  
*Polonium-210, spektrometri alfa, pengesahan kaedah, keteguhan*

### INTRODUCTION

Polonium-210 ( $^{210}\text{Po}$ ) is a radioactive isotope discovered in July 1898 by Maria Sklodowska-Curie. Polonium-210 is a naturally occurring alpha emitter and exists in the environment due to  $^{210}\text{Pb}$  decay within the  $^{238}\text{U}$  decay chain. Being part of the  $^{238}\text{U}$  decay series,  $^{210}\text{Po}$  is ever-present in our environment. Two key processes lead to its spread in the environment: 1) the disintegration of  $^{226}\text{Ra}$  in seawater and 2) the release of  $^{222}\text{Ra}$  from the earth's crust, which disperses radioisotopes through numerous environmental compartments (Matthews et al. 2007). The release of  $^{210}\text{Po}$  into aquifers and ultimately food chains is also caused by industrial operations such uranium mining (Carvalho 2016; Martin & Ryan 2004), phosphate industries, and oil-fired power plants (Boryło et al. 2013; Vaasma et al. 2017). Due to its widespread distribution and potential for human radiation exposure through ingestion and inhalation,  $^{210}\text{Po}$  is one of the most hazardous naturally occurring radionuclides and one of the most significant environmental radionuclides.

The Radiochemistry and Environmental Group is developing an in-house method for detecting  $^{210}\text{Po}$  in soil/sediment samples for testing services as part of the operations to support the Malaysian Nuclear Agency services. In order to measure alpha-emitter radioactivity in the environment using the alpha spectrometry system, reliable and accurate radiochemical separation and detection procedures are crucial.

Method validation verifies how a particular test's analytical process was carried out. The goal of this project is to expand the application of ISO 17025: 2017 to Radiochemistry and Laboratory (RAS) in response to the requirement for method validation in accordance with ISO clauses (7.2.2.1 and

7.2.2.4). A laboratory shall validate non-standard methods, laboratory-developed methods, and standard methods used outside of their intended scope, according to clause 7.2.2.1. While in accordance with clause 7.2.2.4, the laboratory must keep the following validation records: documentation of the validation procedure's use, a list of the prerequisites, an assessment of the method's performance characteristics, the results obtained, and a declaration of the procedure's validity, including a description of its suitability for the intended use. In this work, the robustness of the test technique was evaluated during method validation.

The term "robustness" refers to a measurement of an analytical method's sensitivity in the presence of small variations in the method's experimental conditions. The geometry of the counting disc (square and round form), differences in Fe content that may affect the sufficiency of HAC, contact time during polonium plating on the silver disc, and counting time interval all contributed to the robustness of the procedure. The reporting data was used to assess the robustness of the method.

## MATERIAL AND METHODS

Each radionuclide that emits alpha has a distinctive energy that can be used for their identification. The majority of the radionuclides for alpha particles have a small range of energy, often between 10 and 20 keV, which is close to the resolution of the silicon detector. As a result, chemical separation of the  $^{210}\text{Po}$  radionuclide is required before analysis.

The following steps make up the radiochemical process for  $^{210}\text{Po}$  determination: sample decomposition, preparing alpha sources, and measurement using alpha spectrometry. A soil/sediment sample of around 0.5g is digested using hot acid digestion. The samples are then evaporated with strong HCl, and over a period of four hours at a temperature not more than  $90^{\circ}\text{C}$ , polonium spontaneously deposits on a silver disc. A typical technique for  $^{210}\text{Po}$  determination involves auto-plating  $^{210}\text{Po}$  on a silver disc to prepare an alpha source. However, the radiochemical approach and sample preparation methods employed in the current process has no standard procedure. Therefore, there is always have chances for this procedure to be enhanced or optimised, especially with regard to sample preparation. Specific methodologies for polonium's radiochemical composition has reported previously (Nurrul et al. 2021).

Alpha spectrometry system is used to measure the activity concentrations of alpha emitter radionuclides, including  $^{210}\text{Po}$ . For energy and efficiency calibration, a multinuclide point source ( $^{238}\text{U}$ ,  $^{234}\text{U}$ ,  $^{239}\text{Pu}$ ,  $^{241}\text{Am}$ ) was used, and the samples were counted under the same measuring conditions as calibrated alpha spectrometry system. Known that the sample geometry and the distance between the counting source and the detector can affect the detection efficiency. Alpha Vision was used to analyse each spectrum. For  $^{210}\text{Po}$  determination, the measurement time was 24hrs and counting shelf was the closest to the detector (Shelf no. 1).

Certified reference materials from the International Atomic Energy Agency (IAEA) with a variety of compositions, such CRM IAEA-384 (Povinec et al. 2007), IAEA-385 (IAEA 2008), IAEA-410, and IAEA-412 with a known amount of  $^{210}\text{Po}$ , were used to complete this study. In this investigation, a  $^{209}\text{Po}$  NIST traceable radiotracer with an accessible radioactivity value was used for the recovery check.

## RESULTS AND DISCUSSION

### *Square vs. round shape silver disk geometry*

In order to validate the method of determining polonium, the radioactivity data obtained through alternative counting source geometries (square vs. round shape) were compared in terms of robustness. Before plating, the 99% pure silver disc had been cut into square and round shapes and cleaned with silver polish to remove any oxides or other impurities from its surface.

As demonstrated in Table 1, both data utilising square and round shape geometry for the counting disc were recorded within certified range activity concentration (Bq/kg) with a high recovery value (almost 90%).

Table 1: Set of CRM data using different geometry of the silver disk

Sample Number	Po-210 activity (Bq/kg)	Recovery (%)	Silver disk geometry
1.	28.00	98.56	Round Shape
2.	28.81	96.95	Round Shape
3.	27.81	94.25	Round Shape
4.	27.36	91.80	Round Shape
5.	30.1	91.8	Square Shape
6.	30.8	104.7	Square Shape
7.	29.3	88.9	Square Shape
8.	28.3	90.4	Square Shape

T-test has been used to analyse the method's robustness when using different geometries of the counting source (square vs. round shape). Both square shape geometry and round shape geometry were comparable by > 95% confidence level according to T-test calculations in Table 2.

Table 2: T-test calculation

Statistical analysis	Round shape geometry	Square shape geometry
Mean	27.9963	29.6367
Standard Deviation	0.5237	0.9107
Varian	0.2742	0.8294
Number of replicates	4	4
T-value	3.123024135	
Degree of Freedom	6	
Critical Value based on T distribution table	2.45	
95% confidence level	<0.05	
T-test	0.445	

***Variations in Fe content that may affect the adequacy of hydroxylamine hydrochloride, HAC***

For the conversion of Fe<sup>3+</sup> to Fe<sup>2+</sup>, hydroxylamine hydrochloride (HAC) is added to the plating media as a reducing agent. Environmental samples are known to contain interference ions of manganese (Mn), iron (Fe), selenium (Se), chromium (Cr), or Tellurium (Te) that disrupt the deposition of polonium. Hydroxylamine hydrochloride (HAC) were added to eliminate Fe<sup>3+</sup> that will interfere the deposition of Po<sup>2+</sup> onto silver disc by reduction reaction to Fe<sup>2+</sup>.

The amount of iron (Fe) in the CRM was measured using neutron activation analysis (NAA). The stated amounts of Fe in various CRM were used to demonstrate that just 1 g Hydroxylamine hydrochloride (HAC) used in the developed procedure is required to convert Fe<sup>3+</sup> ions to Fe<sup>2+</sup>. Additionally, by converting Mn<sup>4+</sup> to Mn<sup>3+</sup>, potassium permanganate (KMnO<sub>4</sub>) can be used as a colour indicator to determine how much hydroxylamine hydrochloride is required.

***Fe analysis using Neutron Activation Analysis (NAA)***

Using the idea that an element in the sample emits gamma rays after being bombarded and activated by neutrons at a rate that is directly proportional to its concentration, neutron activation analysis (NAA) was used to determine the amount of Fe in Certified Reference Materials (CRM), IAEA-384, IAEA-385, IAEA-410, and IAEA-412. Samples were placed in a rotating rack within the TRIGA MARK reactor, where Fe identify from 2 energy peaks, which are 1099 keV and 1292 keV using gamma spectrometry. The Fe element content for each CRM is shown in Table 3.

According to Table 4, the computed u-score which is smaller than the suggested value, 1.64 between the experimental value and the certified value of the reference materials IAEA-384, IAEA-385, IAEA-410, and IAEA-412 is recorded as 0.31, 0.03, 0.23, and 0.24, respectively. It can be seen from this that the stated outcome is consistent with what was anticipated (IAEA 2002; Manickam et al. 2010). Based on radioactivity data, the study demonstrated that 1g of HAC supplied during the plating method was sufficient and reliable for reducing Fe<sup>3+</sup> to Fe<sup>2+</sup> in all sediment samples. Applying the desired amount of HAC resulting successfully deposited of the Po<sup>2+</sup> ion on the silver disc (Szarlowicz 2019).

Table 3: Fe content (ppm) in various types of CRM

CRM	FE concentration (ppm)		
	1099 keV	1292keV	AVERAGE
IAEA-384	98.99	89.85	94.42
IAEA-385	30630.65	30599.4	30615.03
IAEA-410	6512.68	6462.33	6487.51
IAEA-412	39211.15	39314.12	39262.64

Table 4: Po-210 measurement data and u-score using certified material IAEA-384, IAEA-385, IAEA-410 and IAEA-412

Certified material	Exp No.	Experimental radioactivity (Bqkg <sup>-1</sup> )	U-score
IAEA-384	1	12.24±4.80	0.31
	2	12.16±3.90	
	3	12.22±3.88	
	AVERAGE	12.21±4.17	
IAEA-385	1	26.02±5.29	0.03
	2	29.5±4.7	
	3	28.06±4.99	
	AVERAGE	27.86±4.99	
IAEA-410	1	222.64±23.64	0.23
	2	208.44±20.72	
	3	216.59±22.32	
	AVERAGE	215.89±22.23	
IAEA-412	1	86.82±13.40	0.24
	2	86.19±12.95	
	3	86.21±11.85	
	AVERAGE	86.41±12.73	

### Plating time

The deposition of polonium was carried out on a silver disc (99% purity) with a diameter 25mm. The silver disc was placed in a holder and immersed in solution for different times. In this experiment, the solution was stirred during the plating time. Based on Table 5, which examined the impact of contact time during Polonium auto-plating, it was determined that a plating period of 4 hours was the ideal amount of time.

Table 5: Radioactivity and FWHM of CRM IAEA-385 measured with different plating time

Contact time	Average <sup>210</sup> Po activity (Bq/kg),N=3	Recovery (%)	Average <sup>209</sup> Po FWHM	Average <sup>210</sup> Po FWHM
2hrs	24.12	69.72	44.72	42.82
4hrs	27.64	90.87	33.44	32.05
8hrs	23.02	92.87	32.54	34.46
16hrs	33.26	45.00	65.60	64.74

According to this study, 4-hour deposition durations result in high quality measurement sources, which yield thin, uniform alpha sources with excellent peak resolution (30 keV) (Figure 1) and <sup>210</sup>Po sample radioactivity readings within the certified value of 26 to 30 Bq/kg. <sup>210</sup>Po is challenging to fit into the certified value after an 8-hour plating process. It is thought that iron has impeded the deposition of polonium. It is well known that some interferences, including ions of Mn, Fe, Se, Cr, or Te, can be found in environmental samples and prevent the polonium from depositing. Due to its high abundance on Earth in terms of mass, iron is the metal that produces the most interference during

the analysis of sediment samples (Szarlowicz 2019). It's also possible that the longer hours spent plating in the acid solution caused the silver disc to start to degrade. Figure 2 illustrates the thick alpha sources, which exhibited the worst peak in resolution at 16 hours of deposition.

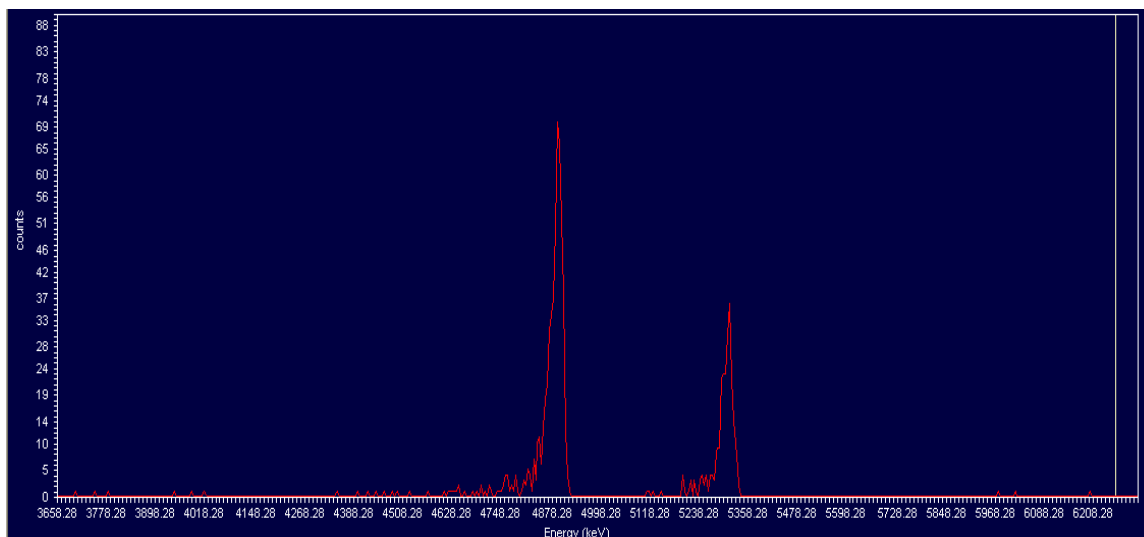


Figure 1: Spectrum with high peak resolution (30 keV)

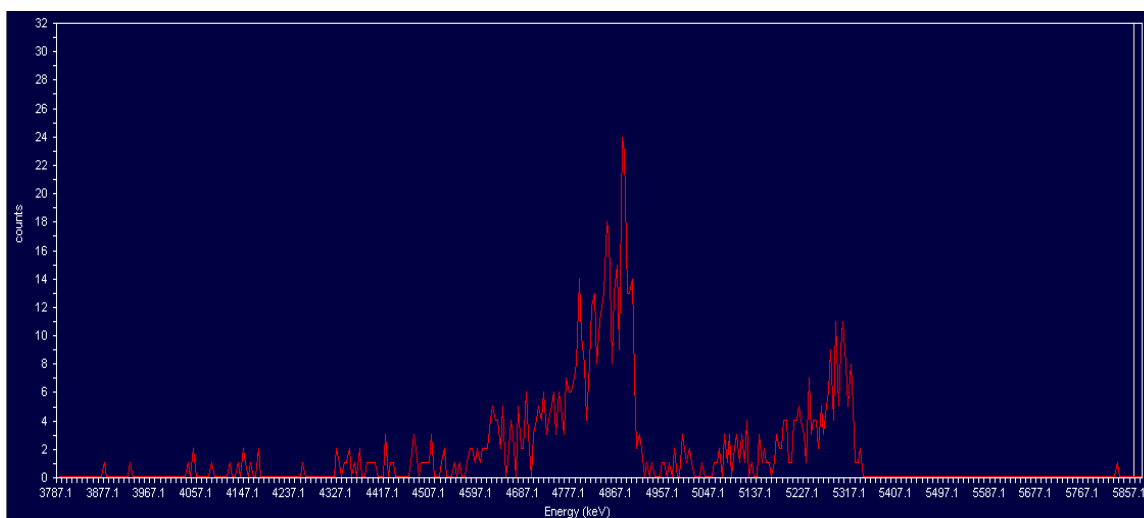


Figure 2: Spectrum with worse peak resolution (60 keV)

### Counting time interval

The activity of CRM IAEA-385 is determined by study at various counting time intervals. Using the same sample preparation source, samples were recounting at day 1<sup>st</sup>, 9<sup>th</sup>, and 21<sup>st</sup> and 60<sup>th</sup> after the separation date. Table 6 displays the measured activity. The method is confirmed to be reliable for measurement time intervals up to 21 days by the U-score analysis, which revealed that the radioactivity measured has no significant difference at different counting time intervals.

Table 6: Radioactivity of CRM IAEA-385 measured at day 1, 9 and 21.

Sample code	Counting date (counting date interval)							
	16/6/2022 (Day 1 <sup>st</sup> )		24/6/2022 (Day 9 <sup>th</sup> )		6/7/2022 (day 21 <sup>st</sup> )		15/8/2022(day 60 <sup>th</sup> )	
	Act	Unc	Act	Act	Unc	Act	Act	Unc
I1	28.52	6.05	27.14	22.01	6.05	27.14	22.01	5.20
I2	27.65	4.87	25.84	25.60	4.87	25.84	25.60	4.87
I3	27.90	4.92	24.67	26.19	4.92	24.67	26.19	4.88
I4	27.64	5.00	28.47	30.51	5.00	28.47	30.51	5.79
I5	27.38	4.55	28.41	27.48	4.55	28.41	27.48	4.96
I8	27.50	4.57	28.15	32.41	4.57	28.15	32.41	5.56
AVERAGE	27.77	4.99	27.11	27.37	4.99	27.11	27.37	5.21
U-Score	0.04		0.17	0.11		0.17	0.11	

## CONCLUSION

The technique employed to detect the activity  $^{210}\text{Po}$  in the environmental samples was determined to be robust. It is discovered that a minimum counting period of 24 hours is adequate to allow the alpha spectrometry to identify  $^{210}\text{Po}$  quantitatively. This measuring methodology is reliable in terms of physical and chemical parameters, according to the method validation; 1) Data employing geometric counting discs of square and round shapes recorded the activity concentration (Bq/kg) within the accepted range value, 2) For all sediment samples, 1g of HAC applied during the auto-plating method was sufficient and reliable to convert  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ , with resulting  $\text{Po}^{2+}$  ion successfully deposited on the silver disc, 3) The optimal plating time for alpha polonium is 4 hours, and during this procedure, thin, uniform alpha sources with excellent peak resolution (30 keV) are created, 4) The radioactivity measured has not significantly different at various counting time intervals up to 60<sup>th</sup> days. In conclusion, this analytical method has shown its robustness in quantifying  $^{210}\text{Po}$  in the samples.

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