Jurnal Sains Nuklear Malaysia, 2013, 25(2): 61-67
ISSN: 2232-0946

A COMPARISON TECHNIQUE OF ALPHA AND GAMMA SPECTROMETRY TO MEASURE ^{210}Pb ACTIVITY IN MARINE SEDIMENT CORE

Zal Uyun Wan Mahmood[1], Yii Mei-Wo[1], Che Abd. Rahim Mohamed[2], Norfaizal Mohamed @ Mohamad[1] and Abdul Kadir Ishak[1]

[1]Radiochemistry and Environment Laboratory, Malaysian Nuclear Agency, Bangi, 43000 Kajang, Selangor, Malaysia
[2]Marine Ecosystem Research Centre, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia
Correspondence author: zaluyun@nuclearmalaysia.gov.my

ABSTRACT

The most commonly used techniques of alpha and gamma spectrometry were performed to measure ^{210}Pb activity in marine sediment core as a comparison. Alpha analytical technique measured the activity of ^{210}Pb from it's in-grow grand-daughter ^{210}Po after a chemical separation, assuming radioactive equilibrium between the two radionuclides. Meanwhile, gamma analysis technique allows direct measurement, non-destructive and no preliminary chemical separation. Through the comparison, it is found that both alpha and gamma analysis techniques were slightly difference. Overall, the results from alpha analytical technique were basically higher than those from the gamma analytical techniques. Some logical argument had been discussed to explain this situation. In routine analysis, the analytical technique used should be chosen carefully based on advantages and disadvantages of the each technique and analysis requirements. Therefore, it is recommended to determine exactly the needs and purpose of analysis and to know the sample history before decide the appropriate analytical technique.

Keywords: Activity, alpha and gamma spectrometry, analytical technique, comparison, marine sediment, ^{210}Pb

INTRODUCTION

Lead-210 (^{210}Pb) ($t_{1/2}$: 22.3 years) occurs naturally as one of the decay products of the ^{238}U series. ^{210}Pb is a very useful tracer and widely for variety applications in marine environment processes. Measurement of ^{210}Pb have found extensive application in the ^{210}Pb geo-chronometry (sedimentation rate, sediment aging, sediment accumulation etc.), assessments of material fluxes to the seafloor, environmental pollution studies and others (Ebaid and Khater, 2006; Zaborska et al., 2007).

A number of analytical techniques are available for the measurement of ^{210}Pb, based on different physical and chemical principles. They differ concerning the reachable detection limit, selectivity, analytical error reproducibility and stability against different chemical composition and levels of others natural radionuclides. There are three commonly used radiometric methods for the measurement of ^{210}Pb activity in the environmental samples, that are a) gamma-ray spectrometry for ^{210}Pb, which allows direct measurement in various media, including water, rocks, soil and sediment; b) beta counter and spectrometry observing the growth of its daughter ^{210}Bi; and c) alpha spectrometry of its grand-daughter ^{210}Po, in both beta and alpha measurement, assuming there is radioactive equilibrium between ^{210}Pb and ^{210}Po (Ebaid and Khater, 2006; Pilleyre et al., 2006). The use of suitable analytical technique should be chosen carefully based on advantage and

disadvantage of the each technique and analysis requirements. Therefore, it is recommended to prior determine the needs and purpose of analysis and know the sample history before decide on the most suitable analytical technique.

The objective of this study was aimed to compare the capability and suitability of different techniques for measuring the activity of ^{210}Pb in marine sediment core using alpha and gamma spectrometry.

MATERIALS AND METHODS

Field Method

Marine sediment core of 100 cm length from Manila Bay was collected in December, 2004 using gravity corer. 0 – 20 cm and 20 – 100 cm of sediment core was sliced at 0 – 2 cm and 0 – 1 cm intervals, respectively. All sediment samples were kept into a pre-weighted air tight sample container and bring to the laboratory for further analyses.

Sample Pre-Preparation

All sediment samples were dried in an oven at 60^{o}C until a constant weight. Then, the dried sediments were crushed, ground into fine particles, sieved through 125 µm sieve mesh size for homogenous.

Analytical Techniques for the Determination of ^{210}Pb

Alpha analysis: Radiochemical separation of ^{210}Po was performed on 0.5 g dried sediments samples. The samples were spiked with 25 – 50 mBq of ^{209}Po tracer as analytical yield and digested on the hot plate with 30 mL of HNO_3, 5 mL of $HClO_4$ and 10 mL of HCl at temperature below 70^{o}C until dryness (Tee et al., 2003; Wood et al., 1997). Residue were then been dissolved in a 0.5 M HCl acid solution. Any un-dissolved materials were filtered-off. Then, polonium isotopes in the solution were spontaneously plated for 4 hours on a silver disc after adding ascorbic acid to prevent Fe deposition (Al-Masri et al., 2002). ^{210}Pb activities were determined through its granddaughter (^{210}Po) with one day of alpha spectrometry counting during secular equilibrium stage (Henderson et al., 1999; San Miguel et al., 2004; Wood et al., 1997). The quality control for this procedure was performed using the International Atomic Energy Agency (IAEA) standard reference material (IAEA- 315 and IAEA-326).

Gamma analysis: About 3 – 5 g of homogenous sample was transferred into the 7 mL polyethylene containers and sealed. The specific activities of ^{210}Pb were measured using CANBERRA well-type gamma spectrometry for 24 hours. The activities of ^{210}Pb were determined from the measurement of its photopeak at energy of 46.54 keV. The energy and efficiency of counting system was calibrated using a mixed standard source as reported earlier by Yii et al. (2007), meanwhile quality control was performed using the International Atomic Energy Agency (IAEA) standard reference material (IAEA- 326) on the same counting geometry. Recommended values of ^{210}Pb activity at 95% confidence interval in two selected reference materials are given in Table 1.

Table 1: Recommended value of ^{210}Pb activity of (Bq/kg dw.) as reported in certificate of certified reference materials for IAEA-315 and IAEA-326

CRM	^{210}Pb Activity (95% Confidence Interval) (Bq/kg)	Reference Date
IAEA-315	30.10 (26.60 – 33.70)	01-01-1993
IAEA-326	53.30 (48.80 – 57.80)	31-12-1994

RESULTS AND DISCUSSION

Comparison of Measurement Technique for the Determination of ^{210}Pb in Marine Sediment Core

Comparison of the two different analytical techniques used in the determination of ^{210}Pb activities found that results from both alpha and gamma analysis techniques were slightly difference (Figure 1). The alpha spectrometry results reflected higher than that obtained by gamma spectrometry. On the other hand, the ^{210}Pb measurements observed a trend of higher activities by alpha spectrometry but the errors connected to these measurements was quite small of 5% compared to 11% for gamma spectrometry. A systematic error issue between measuring techniques was also noticed by Tanner et al. (2000). Also, low branching ratio value (which about 5%) used in gamma spectrometry for calculation of ^{210}Pb could be another main contributor to this phenomenon (LBNL, 1999).

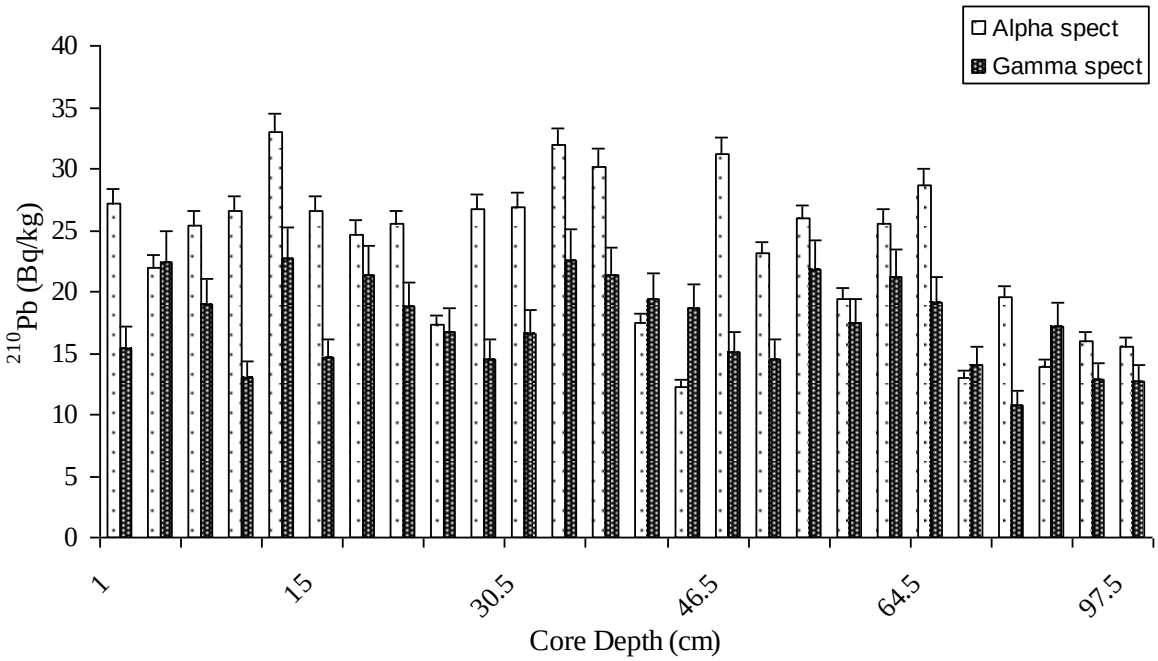

Figure 1: Activities of ^{210}Pb in marine sediment core measured by alpha and gamma spectrometry

The differences of both methods could be explained by the unexpected self attenuation in samples measured using gamma spectrometry. Accordingly, careful efficiency calibration should be carried out to elude this problem. On the other hand, another issue concerning self attenuation problem

should also be considered, where empirical and experimental methods could be used to take the self attenuation in the lower energies region into consideration (Cutshall et al., 1983; Ebaid and Khater, 2006). Small volume of about four grams of sediment samples used in gamma spectrometry counting could also be another contributing factor. Aligned to small volume of samples, insufficient counting time for measuring the ^{210}Pb activity by the gamma technique also possible observed differences between alpha and gamma spectrometry results. All these factors may lead to inaccuracies in ^{210}Pb measurement. Since, it is well known that gamma spectrometry measurements always performed using large size of samples, so, the homogeneity issue was not bother the analysis. Furthermore, this might be lifted up the activities of ^{210}Pb.

Some of the observed differences between alpha and gamma might be explained by environmental factors such as patchiness of sediment properties among depth interval or layer of sediment. Insufficient precision in slicing and combining sediment intervals for analyzing by the gamma technique is another possible explanation for observed differences. It also could be looked like the different behaviors of ^{210}Pb and ^{210}Po in alpha measurement. (Zaborska et al., 2007).

The above differences were supported by statistical analysis that have medium positively correlation between alpha and gamma spectrometry in terms to determine the activity of ^{210}Pb in marine sediment core, whereas correlation coefficient, r was 0.606 (Figure 2). It was due to the homogeneity issue may be a major factor, in addition to the necessity of sample self attenuation correction that was inaccuracy in all of results.

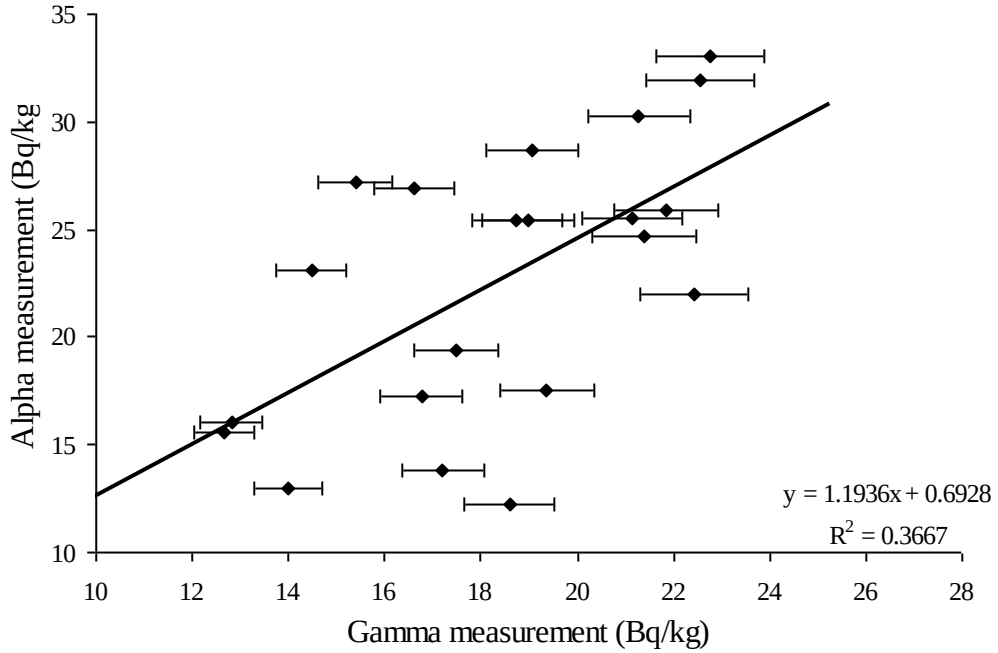

Figure 2: Correlations between the activities of ^{210}Pb in marine sediment core measured by both spectrometry of alpha and gamma

Comparison of Counting Parameters for the Measurement of ^{210}Pb in Marine Sediment Core

Detailed comparison of counting parameters of the two different analytical techniques of alpha spectrometry and gamma spectrometry is given in Table 2. There are obvious differences observed between alpha and gamma spectrometry background counting (cpm) and minimum detectable

activity (MDA)(Bq/kg). This shows that alpha spectrometry can achieve lower MDA and background counting compared to gamma spectrometry.

Concerning the duration of the ^{210}Pb complete analysis, a gamma analysis needed only 4 days to prepare the sample including drying, grinding, sieving and others processes prior to counting. While else for alpha spectrometry, the complete analysis duration depends on the chosen analytical techniques. It took at least 10 days for sample preparation, dissolution, separation, auto-spontaneously plating and counting.

Table 2: Counting parameters for the measurement of ^{210}Pb in marine sediment core using alpha and gamma spectrometry

Technique	Alpha Spectrometry	Gamma Spectrometry
Sample volume/size (g)	0.5	3 – 5
Duration of sample preparation, analysis and measurement (day)	10	4
Counting time (minutes)	1440	1440
Background, cpm	0.004	2.0
Relative Counting efficiency, %	11	25
Minimum detectable activity, MDA (Bq/kg)	0.0005	2.5

Advantages and Disadvantages of Techniques

To guarantee the comparability of the results from these two different analytical methods, the advantages and disadvantages of each method can be lined as follows:

Alpha Spectrometry

Advantages: The main advantages are the superior in precision and this make it more suitable for small sample size. It also have excellent low limit of detection and MDA.

Disadvantages: The disadvantages of analysis ^{210}Pb using alpha spectrometry are that the time delay before analysis. However, it is depend on ^{210}Pb-^{210}Po secular equilibrium condition in the sample. Referred to the purpose of reaching secular equilibrium, the sample required to be stored for at least two years, especially for those samples with expected higher ^{210}Po activity than that of ^{210}Pb (Ebaid and Khater, 2006). Moreover, alpha spectrometry technique is characterized by a time consuming separation process and require careful chemical treatment that was considered to be the main disadvantages of this technique (Jia et al., 2000; Vesterbacka and Ikaheimonen, 2005). Part from that, the alpha technique is based on indirect ^{210}Pb measurement, where the activity of ^{210}Pb was determined through its daughter, ^{210}Po. In some cases, using a relatively small size of the sample for alpha spectrometry analytical techniques could also increase the analytical error due to the in-homogeneity sample. (Ebaid and Khater, 2006)

Gamma Spectrometry

Advantages: The main advantages are being fast, nondestructive, relatively simple sample preparation because usually do not require preliminary chemical separation and direct analysis without delaying through the measurement of 46.5 keV gamma energy transition (Ebaid and Khater, 2006). On the other hand, gamma spectrometric analytical technique was also easier, time

efficient, needs less man power and cost when compared to the other techniques; and also, it can measure a several gamma emitting radionuclides simultaneously in an individual sample.

Disadvantages: The main disadvantage is that the detector requires liquid nitrogen to cooling in order to be workable. When using gamma technique, there is also possibility of error due to self absorption (Cutshall et al., 1983) and usually high measurement errors were associated with the technique. In some cases, when a sample is expected to have a relatively low activity of ^{210}Pb, a large volume of sample and additional counting time was required. Furthermore, measured samples need to be in the same geometry and characteristics with standard reference material and calibrating materials used. Another disadvantage is it relatively high MDA and the difficulty to perform corrections for self attenuation in the sample matrix (Cutshall et al., 1983). However, its necessity to correct the counting efficiency for the gamma ray attenuation due to sample matrix and composition in order to achieve a good measurement (Ebaid and Khater, 2006).

CONCLUSIONS

Two most commonly used techniques, alpha and gamma spectrometry were performed to measure ^{210}Pb activity in marine sediment core. Through the detailed comparison, it is found that there were slightly difference in both alpha and gamma analysis techniques. Alpha spectrometry technique shows good accuracy with activity of ^{210}Pb generate analytical yield of more than 80%. Moreover, it was better and more precision technique and for marine sediment core to achieve low MDA. Gamma spectrometry meanwhile has higher error and larger MDA but the advantage of rapid and non destructive compared to alpha. In routine analysis, the analytical technique used should be chosen carefully based on advantage and disadvantage of the each technique and the analysis requirements. Therefore, it is recommended to determine exactly the needs and purpose of analysis and to know the sample history in order to decide the appropriate analytical technique.

ACKNOWLEDGEMENTS

The authors would like thanks to the POME members for sampling and sample preparing through the Scientific Activities of POME in the JSPS Multilateral Core University Program. Thanks also to the Universiti Kebangsaan Malaysia and Malaysian Nuclear Agency members for their helping during the samples analysis and paper writing.

REFERENCES

Al-Masri, M.S., Mamish, S. and Budier, Y. (2002). The impact of phosphate loading activities on near marine environment: the Syrian coast, *J. Environ. Radioact.* 58: 35-44.

Cutshall, N.H., Larsen, I.L. and Orslen, C.R. (1983). Direct analysis of ^{210}Pb in sediment samples: self absorption corrections, *Nucl. Instr. Meth*. 206: 309-312.

Ebaid, Y.Y., and Khater, A.E.M. (2006). Determination of ^{210}Pb in environmental samples, *J. Radianal. Nucl. Chem*. 270 (3): 609-619.

Henderson, G.M., Lindsay, F.N. and Slowey, N.C. (1999). Variation in bioturbation with water depth on marine slopes: a study on the Little Bahamas Bank, *Marine Geol.* 160: 105-118.

Jia, G., Belli, M., Blasi, M., Marchetti, A., Rosamilia, S. and Sansone, U. (2000) ^{210}Pb and ^{210}Po determination in environmental samples, *Appl. Radiat. Isot.* 53:115-120.

Lawrence Berkeley National Laboratory (LBNL). 1999. Source from "The Lund/LBNL Nuclear Data Search Version 2.0, February 1999" website http://nucleardata.nuclear.lu.se/nucleardata /toi/., Accessed on 11th January 2010.

Miguel, E.G.S., Bolivar, J.P. and Garcia-Tenorio, R. (2004). Vertical distribution of Th-isotope ratios, ^{210}Pb, ^{226}Ra and ^{137}Cs in sediment cores from an estuary affected by anthropogenic releases, *Sci. Total Environ*. 318: 143-157.

Tanner, P.A., Pan, S.M., Mao, S.Y. and Yu, K.N. (2000). γ-Ray spectrometric and α-counting method comparison for the determination of Pb-210 in estuarine sediments, *Appl. Spectro.* 54:1443-1446.

Tee, L.T., Ahmad, Z. and Mohamed, C.A.R. (2003). Estimation sedimentation rates using ^{210}Pb and ^{210}Po at the coastal water of Sabah, Malaysia, *J. Radioanal. Nucl. Chem.* 256(1): 115-120.

Vesterbacka, P. and Ikaheimonen, T.K. (2005). Optimization of ^{210}Pb determination via spontaneous deposition of ^{210}Po on a silver disk, *Anal.Chim. Acta*. 545: 252-261.

Wood, A.K.H., Ahmad, Z., Shazili, N.A.M., Yaakob, R. and Carpenter, R. (1997). Geochemistry of Sediments in Johor Straits between Malaysia and Singapore, *Cont. Shelf Res.* 17(10): 1207-1228.

Yii, M.W., Zaharudin, A. and Norfaizal, M. (2007) Concentration of radiocaesium ^{137}Cs and ^{134}Cs in sediments of the Malaysian marine environment, *Appl. Radiat. Isot.* 65: 1389-1395.

Zaborska, A., Carroll, J-L., Papucci, C. and Pempkowiak, J. (2007). Intercomparison of alpha and gamma spectrometry techniques used in ^{210}Pb geochronology, *J. Environ. Radioact*. 93: 38-50.