

γ -Ray Spectrometric and α -Counting Method Comparison for the Determination of Pb-210 in Estuarine Sediments

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An intercomparison of methodology and of dating results, from α -counting and from the more recent γ -spectrometry method, has been made for marine sediment cores from several locations. The former method involves considerable chemical manipulation, whereas the latter is more straightforward and enables direct interpretation of the results. Similar precisions (~12%) were found for both methods. With the constant flux model, the methods gave calculated sedimentation rates between 4.3 and 7.8 cm a⁻¹ for replicate cores near a ferry pier in Hong Kong Harbor. The γ -spectrometry method is thus a reliable, more rapid method for routine monitoring and investigation of the harbor dynamics and history of pollution.

Index Headings: Analytical methods; Gamma-ray spectrometry; Alpha spectrometry; Marine sediment pollution.

INTRODUCTION

Pb-210 (half-life 22.3 years) has been widely used as an environmental tracer for studying sediment deposition in different sedimentary environments^{1,2} and in marine pollution studies.³⁻⁵ It is essential that accurate values for Pb-210 activities be determined for sediment samples in order to set up the geochronology for pollutants deposited in sediments.

Pb-210 in sediment samples can be detected and determined via its β -active daughter nuclide, Bi-210,⁶ or its α -active granddaughter, Po-210,⁷ and also by direct measurement of Pb-210 in samples from its 46.5 keV γ -particle emitted with a probability of 4%.⁸⁻¹⁰ Due to the complexity of the wet chemistry involved, the measurement of Pb-210 via Bi-210 has been used by very few researchers. A methodology for Pb-210 dating and sediment geochronological studies based on Po-210 α -particle spectrometry has been established at Nanjing University.¹¹ In order to ensure the continuing accuracy of laboratory results, this laboratory has become a participant of the IAEA standard reference material calibration, with results shown in the Appendix, which is in table format. Previous studies of sedimentation rates based on γ -ray spectrometry have been carried out at City University of Hong Kong.¹²

In particular, the α -particle spectrometry method requires chemical extraction of Po-210 from the sediments and necessitates a knowledge of the chemical yield of Po-210. Sample preparation is thus time- and effort-consuming, and the precision of the method can be greatly affected by the quality of the operations and/or the uniformity of experimental conditions. By contrast, the γ -

ray spectrometry method enjoys the advantages of much easier sample-preparation procedures and more straightforward and direct interpretation of the results. It is much less dependent on the operations, and the experimental conditions are comparatively much easier to maintain. The drawbacks of the γ -ray spectrometry method were the low energy of γ -rays (46.5 keV) from Pb-210 and the low branching ratio (4%), which made detection of these γ -rays rather difficult with early-generation γ -ray spectrometers. These problems have been overcome by using the n -type high-purity germanium (HPGe) detectors now available.

In this paper we present an intercomparison of the dating results from the use of the Po-210 and γ -ray methods at these two laboratories. The Pb-210 activities have been measured for several sediment samples from three estuaries. The aim of the study is determine the relative precision and comparability between the two methods when the same counting time is used.

MEASUREMENT METHODOLOGY

Sediment Samples. Samples were collected by gravity core or vibrocores from three estuaries: (1) Xiamen Harbor, Fujian Province, China; (2) Jiaojiang Estuary, Zhejiang Province, China; (3) Victoria Harbor, Hong Kong. The sediment samples were dried at 105 °C, ground to fine powder, and then homogenized thoroughly. All samples were stored in sealed containers in the laboratory for more than one year. This approach enabled the achievement of secular equilibrium between Ra-226, Rn-222, and the Rn daughters such as Bi-214 and Pb-214.^{13,14}

Po-210 α -Counting Method. The analytical procedure takes advantage of the fact that, within two years, secular equilibrium is achieved between Pb-210 and its granddaughter Po-210 in the sediment, so that both isotopes are at the same activity level. The sediment was analyzed by the methods outlined by Flynn⁷ for the α -emitting isotope Po-210. After drying and homogenization, Po-208 was added as a tracer to the sediment to determine the chemical recovery and plating efficiency. The dried sediment (~1–2 g) was then digested in a Teflon[®] bomb, with concentrated nitric and hydrochloric acids, for 8 h in a water bath at 95 °C. The nitric acid was removed by boiling the digested sediment to dryness in a Teflon[®] beaker. The final residue was taken up in the plating solution of 0.5 M HCl. Before plating, any remaining undissolved sediment was removed by centrifuging the sample. The polonium plated with an efficiency of 90–95% after 6 h, onto one side of the nickel disk in the 0.5 M HCl solution at 85 °C. The plates were counted for approximately 24

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TABLE I. Activities of natural radionuclides in the standard sample (20.91 g) for γ -ray spectrometry dating of sediment.

Radionuclide	Pb-210	Th-234	Pb-214	Bi-214	Th-232	K-40
Activity (Bq/20.91 g)	6.38	6.57	6.38	6.38	2.926	10.99

h on an Ortec dual α -spectrometer interfaced with a multichannel analyzer. The Po-208 activity was used to calculate the chemical and counting efficiency.

γ -Spectrometry Method. The measurement of 46.5 keV γ -rays from Pb-210 has the major advantage that it permits simultaneous determination of Ra-226, as well as certain other nuclides such as Cs-137. However, a previous study of Hong Kong marine sediments has found that the Cs-137 dating method yields results that are subject to external disturbance to a greater extent and is less reliable than the Pb-210 method.¹² An *n*-type HPGe low-background γ -ray spectrometer was used. The coaxial detector with a lead shield 10 cm thick has an efficiency of 25%. The system is connected to an IBM PC multichannel analyzer, with 4096 channels and a gain of 0.488 keV per channel. The resolution of the 1.33 MeV γ -ray peak from Co-60 is 1.89 keV, and the integrated background from 25 keV to 2 MeV is 1.5 cps. In this method, 20.91 g of sediment was placed in a thin petri dish of 10 cm diameter, directly on top of the detector. Each sample was measured for 24 h, and the results analyzed using the GRD 5.1 software.

The γ -ray method requires the preparation of standard and background samples. The ingredients of the basal material chosen to make up these samples were based on the chemical composition of the certified reference material BCSS-1 (coastal marine sediment: National Research Council, Canada), with the following amounts (wt %): SiO₂, 66.1; Al₂O₃, 11.83; MgO, 2.44; CaO, 0.76; NaCl, 2.72. These basal materials have very low radionuclide concentrations and have density and γ -ray absorption characteristics¹³ similar to those of the sediment samples to be measured. They were homogenized and dried at 105 °C in an oven to constant mass. The standard sample contained known amounts of natural radionuclides, in addition to the basal materials; the total mass (20.91 g) of the standard sample contained 0.0471 g uranium-radium; 0.2339 g thorium; 0.673 g potassium. The activities of the natural radionuclides in the standard sample are listed in Table I.

RESULTS AND DISCUSSION

The Pb-210 specific activities for various sediment samples from three estuaries are listed in Table II. The coefficients of variation ($100 \times$ standard deviation/mean) of the two different methods are similar, with mean values of 11.8% (α -method) and 12.9% (γ -method). It should be noted that these values were obtained with the use of the same measurement times for both methods. Values near 5% could be obtained from both methods with longer counting times. These results show that measurements based on Po-210 and γ -ray spectrometry can yield Pb-210 values of similar precision. However the Pb-210 specific activities determined from the γ -ray spectrometric method were all larger than those from the Po-210 method. The Wilcoxon signed rank test shows that

TABLE II. Pb-210 specific activities for sediment samples determined by the α -counting and γ -ray spectrometry methods.

Sediment sample ^a (core depth in cm)	Pb-210 (dpm g ⁻¹)	Pb-210 (dpm g ⁻¹)
	α -method	γ -method
Xia 06 (4-5)	5.11 ± 0.49	5.41 ± 0.49
Xia 06 (18-19)	4.47 ± 0.44	4.82 ± 0.48
Xia 06 (30-40)	3.33 ± 0.34	3.93 ± 0.41
Xia 06 (158-162)	1.93 ± 0.21	3.61 ± 0.41
Xia 06 (600-800)	1.89 ± 0.19	2.21 ± 0.45
Jiao 3 (24-30)	2.75 ± 0.30	2.97 ± 0.34
Jiao 5 (25-30)	3.15 ± 0.44	4.34 ± 0.47
Jiao 5 (35-40)	2.92 ± 0.36	3.44 ± 0.38
Jiao 6 (5-10)	2.35 ± 0.31	3.63 ± 0.43
Jiao C2 (suspended material)	3.45 ± 0.37	3.75 ± 0.33
VB39A (0-5)	2.48 ± 0.28	3.24 ± 0.36
VB39A (20-25)	2.82 ± 0.34	5.34 ± 0.48
VB39A (30-35)	2.47 ± 0.28	2.82 ± 0.36
VB39A (70-80)	1.31 ± 0.19	1.74 ± 0.36
VB39A (90-100)	2.81 ± 0.38	3.78 ± 0.42
VB39A (120-130)	1.21 ± 0.16	1.44 ± 0.36
VB39A (190-200)	1.93 ± 0.24	1.98 ± 0.30

^a Xia from Xiamen Harbor; Jiao from Jiaojiang estuary; VB39A from near Stonecutters Island, Hong Kong.

there is a statistically significant difference between the two data sets ($P < 0.0001$, $N = 17$). This means there is a systematic error between the methods employed in the different laboratories. We consider this to be in an acceptable range since the ratios lie between 1.02 and 1.89, with a mean value of 1.29. The relationship between the data sets is shown graphically in Fig. 1. If we reject the outlying data point for VB39A (shown as an open circle), and perform a linear least-squares fit, then the slope is 0.96 ± 0.12 , with an intercept of 0.72 ± 0.34 (dpm g⁻¹), and a correlation coefficient, $R = 0.91$ ($N = 16$). The intercept represents the difference between the two sets of results and arises from the different standard materials used in the two laboratories. The data quality therefore

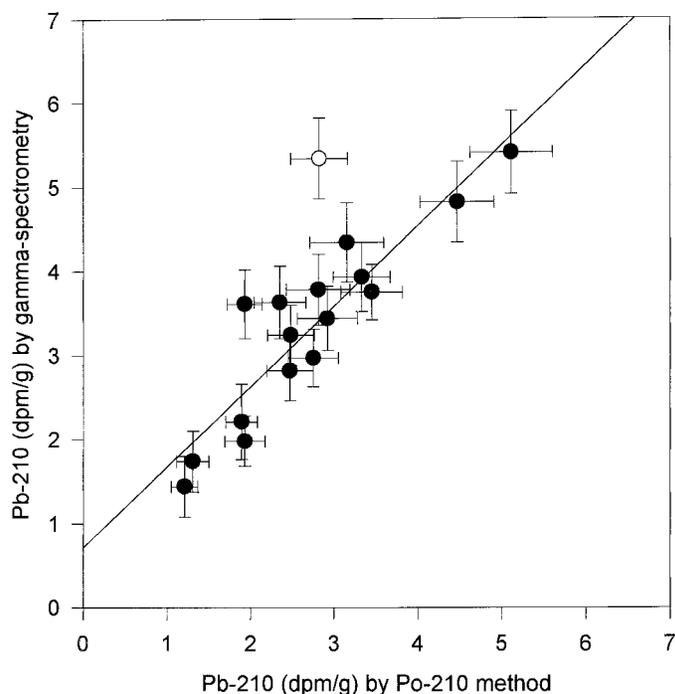


FIG. 1. Plot of Pb-210 specific activities of estuarine sediments (Table I) measured by γ -ray spectrometry and α -counting.

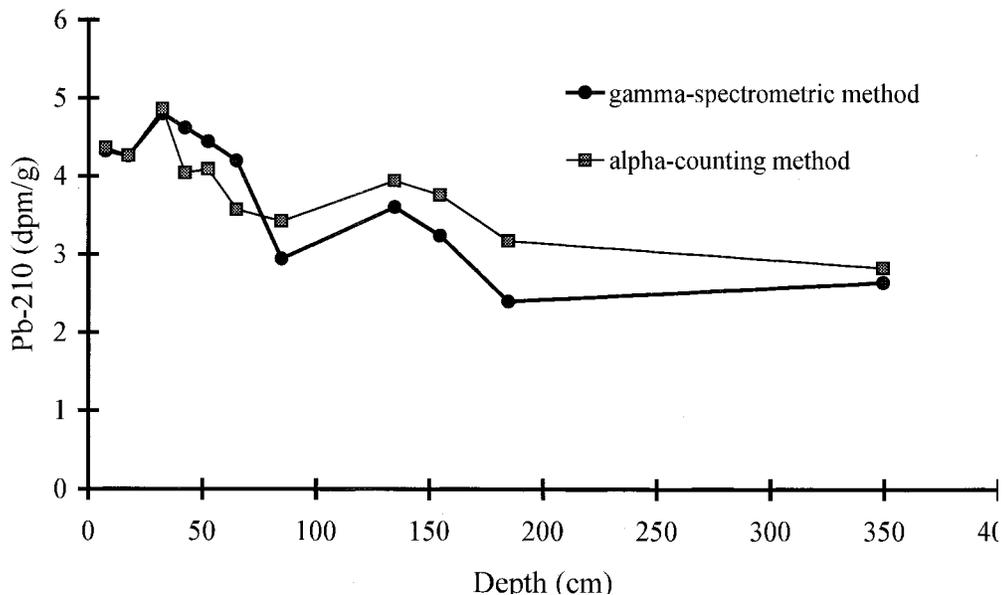


FIG. 2. Comparison of Pb-210 distribution along the core KPV26A from near the Star Ferry Pier, Hong Kong, measured by γ -ray spectrometry and α -counting.

varies with the measurement method, and the Pb-210 standard sample is an important factor affecting the accuracy between the two methods. In the present exercise, the standard was not intercalibrated, and we recommend this procedure for future intercomparisons.

It is interesting to compare the derived sedimentation rates for the 6 m long vibrocore KPV26A, taken from the Star Ferry Pier, Kowloon, Hong Kong. The background Pb-210 activity was taken from the average Ra-226 specific activity in the lower part of the core, as measured by γ -ray spectrometry. Measurements were taken along the core section by direct γ -ray spectrometry at City University and by α -particle spectrometry at Nanjing University. In Fig. 2 a very similar Pb-210 specific activity distribution for this core is observed, with the

use of the two measurement methods. The background was taken as the average Ra-226 measurement in the lower part of the core, from γ -ray spectrometry (2.3 dpm g^{-1}). With the constant flux model,¹⁵ the sedimentation rate for the core KPV26A was calculated to be 4.3 cm a^{-1} ($N = 12, R = 0.73$) by the γ -ray method; and 7.8 cm a^{-1} ($N = 12, R = 0.89$) by the α -counting method. The deviation of each method from the mean result of 6.1 cm a^{-1} is thus around 30%. A replicate core, KPV26B, was taken only 5 m distant from the location of KPV26A. This core was also measured by α -particle spectrometry at Nanjing University. The excess Pb-210 activity for this core decreases approximately exponentially as a function of sediment depth down to 2.5 m, as illustrated in Fig. 3. From the linear least-squares regression fit of the ex-

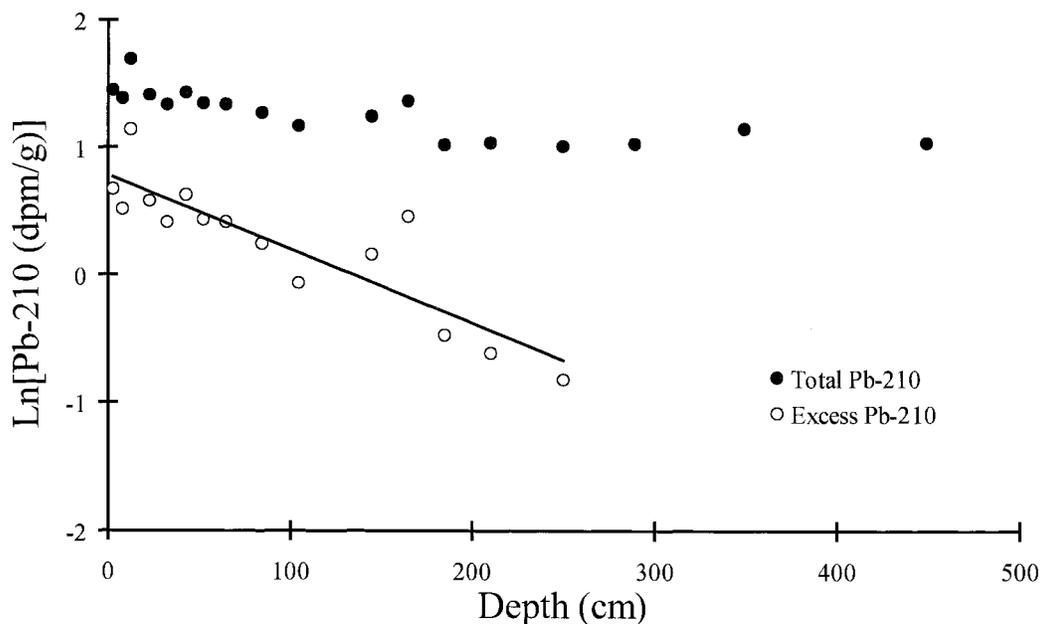


FIG. 3. Total and excess Pb-210 along the core KPV26B as determined by α -counting.

cess Pb-210 activity, the sediment accumulation rate is calculated as $3.3 \text{ g cm}^{-2} \text{ a}^{-1}$, giving the sedimentation rate of $5.3 \pm 0.8 \text{ cm a}^{-1}$ for this part of the core. The trace metal profiles within the core KPV26A decrease to baseline values at a core depth around 5 m, whereas Ca shows an increase below this depth. This result is taken to show the zone of anthropogenic influence, following the construction of the "finger type" Ferry Piers in 1906. From this historical data we would deduce an average sedimentation rate of 5.2 cm a^{-1} .

CONCLUSION

Measurements based on Po-210 α -counting and γ -ray spectrometry can yield comparable values for Pb-210 specific activities. The coefficient of variation of each method was about 12%. The dating of the core KPV26 again indicated similar errors ($\sim 30\%$) in the method results for the derived sedimentation rate. The deviation of the results for the sedimentation rate from replicate cores dated by the Po-210 α -counting method from the mean value was about 10%. Guidelines for the establishment of a quality assurance program in a radioactivity analytical laboratory have previously been given.¹¹ An improvement in the systematic errors present in the results of the present study could be achieved by laboratory intercalibration of the standard and background samples.

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APPENDIX. Results of Pb-210 measurements on IAEA reference materials at Nanjing University Isotope Laboratory.

Sample	Measured value at Nanjing Univ. (Bq kg ⁻¹ DW) ^a	Median of accepted lab values (Bq kg ⁻¹ DW) ^a	Confidence interval ($\alpha = 0.05$)
IAEA-368 marine sediment	23.4 ± 1.3	23.2	19.8–27.2
IAEA-134 marine cockle flesh	4.1 ± 0.8	4.9	4.1–6.7
IAEA-135 marine sediment	48.7 ± 2.7	48.4	43.3–54.1

^aDW = dry weight.