# **Determination of 210Pb in environmental samples**

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Measurement of <sup>210</sup>Pb has gained a highly scientific attention due to its wide range of environmental applications. The most commonly used analytical techniques: gamma-spectrometry, beta-counting and alpha-spectrometry were used to measure environmental samples (geological, soil, sediment). Our paper is aiming at comparing the capabilities and limits of application of these three different analytical techniques for <sup>210</sup>Pb measurement in various environmental samples. In addition, analytical data of <sup>210</sup>Pb measurements with the three different techniques (gammaspectrometry, beta-counting and alpha-spectrometry) are discussed to highlight the degree of comparability and the most probable sources of discrepancies and errors. Based on the demanded investigation, one analytical technique will be chosen for routine analysis, while the other techniques, if they are available, could be used for analytical quality assurance measures. It was essential to compare the analytical efficacy of each technique, which differ concerning the detection limit (MDA), sensitivity, analytical effort, the duration of analysis and waiting time before analysis.

### **Introduction**

Lead-210 is a very useful radioactive element for environmental studies. Measurements of <sup>210</sup>Pb have found extensive applications in the <sup>210</sup>Pb geochronometry (measuring the sedimentation rates) of rapidly accumulating sediments in lakes, estuaries and the coastal marine environments.<sup>1–10</sup> Measurement of 210Pb in air and in surface soils will afford quantitative information about the flux of radon gas  $(^{222}Rn)$  and its daughters in the atmosphere.<sup>11–16</sup> It can help in uranium</sup> exploration and monitoring the transfer of radionuclides of uranium series in soils and aquatic systems. In the context of luminescence dating, the  $^{210}Pb^{226}Ra$  activity ratio can give the proportion of  $222$ Rn that can escape from a given sediment, such data being important in the calculation of annual radiation dose rate. Also, 210Pb and its grand-daughter radionuclide  $(^{210}Po)$  are included in the group of most highly toxic radioisotopes and provide the major internal natural radiation dose to man. It is approximately 18% of the average dose to the population from internal irradiation due to ingested radionuclides. For some members of the public the dose due to ingestion of 210Pb and 210Po may be far higher due to high intakes of specific foodstuffs such as shellfish. $17-19$ 

Lead-210  $(T_{1/2} = 22.2 \text{ y})$  occurs naturally as one of the decay products of the  $238U$  series. Disequilibrium between  $^{210}Pb$  and its parent nuclide,  $^{226}Ra$  $(T_{1/2} = 1600 \text{ y})$ , arises through the diffusion of the intermediate gaseous isotope,  $^{222}$ Rn ( $T_{1/2}$  = 3.8 d). A fraction of 222Rn atoms diffuse into the atmosphere and

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its decay products (mainly  $^{210}Pb$  and its daughter  $^{210}Po$ ) are removed from the atmosphere by wet and dry deposition.<sup>18</sup>

Lead-210 decays by combined emission of weak beta- and gamma-rays and internal conversion electrons to the ground state of <sup>210</sup>Bi ( $T_{1/2}$  = 5 d), which in turn decays by emission of beta-particles to a pure alphaemitter  $2^{10}P_0$  (Fig. 1). Because of the significant selfabsorption of the weak beta-particles of  $^{210}Pb$  and  $^{210}Bi$  $(E_{\beta max} = 16$  and 63 keV, respectively) and the alphaparticles of <sup>210</sup>Po (5.3 MeV), <sup>210</sup>Pb measurements frequently need lead and polonium radiochemical separation prior to their individual analyses.<sup>20</sup>

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 effort, reproducibility and stability against differing chemical composition and levels of other natural radionuclides. There are three commonly used radiometric methods for 210Pb measurement in the environmental samples, which are gamma-ray spectrometry of 210Pb, which allows direct measurement in various media, including water, rocks, soil and sediment; beta counter and spectrometry, observing the growth of its daughter  $^{210}$ Bi; and alphaparticle spectrometry of its grand-daughter <sup>210</sup>Po, assuming radioactive equilibrium between the two radionuclides.18,19,22

A systematic view of methodical principles and details of the 210Pb measurement methods is a prerequisite to compare the analytical power of the different techniques, to guarantee the comparability of the results from these different methods and to know the probable sources of data discrepancies and errors.<sup>19</sup>

This work is aimed at comparing the capabilities of different techniques (gamma-spectrometry, beta-<br>counting and alpha-spectrometry) for <sup>210</sup>Pb counting and alpha-spectrometry) for determination and their limits of application for the purposes of environmental samples analyses.

### **Experimental**

### *Sample preparation*

The first step of analysis involves the drying of the sample matrix at an oven temperature lower than 100 °C, crushing, grinding and sieving through 2 mm sieve mesh size. For ashing, 10 grams of the dried sample was moistured with nitric acid  $(HNO<sub>3</sub>)$  till no further reaction occurs. The sample was dried on a sand bath then ashed at 550 °C for 6–8 hours. If the sample residue was not free of organic carbon, which can be recognized by a dark brown or black colored ash, the ashing process had been repeated again. Finally the sample ash was ground and homogenized.

# *Analytical techniques for the determination of 210Pb in environmental samples*

*Gamma-spectrometry:* The dried samples were transferred to polyethylene containers of  $100 \text{ cm}^3$ capacity. Lead-210 specific activities were measured using well calibrated gamma-spectrometry based on hyper pure germanium (HpGe) detectors. The HpGe detector had a relative efficiency of 40% and full width at half maximum (FWHM) of  $1.95 \text{ keV}$  for  $^{60}Co$ gamma-energy line at 1332 keV. The gamma transmissions used for activity calculations was 46.5 keV with a branching ratio of 4.05%. The gammaspectrometers were calibrated using <sup>210</sup>Pb standard solution in the same sample–detector geometry.<sup>23</sup> The lower limit of detection, with 95% confidence, is 0.44 Bq for 1000 minute measuring time. $^{24}$ 

*Beta-counting:* One milliliter of Pb<sup>2+</sup> carrier (20 mg/ml) is added to 3–5 g of the ashed sample and then dissolved using mineral acids  $(HNO<sub>3</sub>, HF and)$  HCl). Lead is leached with hydrobromic acid (HBr) as tetrabromo-complex, extracted with trioctylamin/toluene and back-extracted with HCl. After addition of  $Bi^{3+}$ carrier,  $Bi^{3+}$  traces are separated by precipitation as BiOCl. Finally lead is precipitated as  $PbCrO<sub>4</sub>$  and collected on a filter paper. The chemical recovery of 210Pb on the filter was determined gravimetrically. After waiting for 8–10 days, the filter is covered with a filter paper of equal size to hold back the low energy betaparticles of 210Pb and the alpha-particles of ingrown  $^{210}$ Po. The high energy beta-particles of  $^{210}$ Bi (1.2 MeV) are counted using a calibrated low background gas proportional counter. The counter was calibrated using 210Pb standard solution sources prepared in the same condition as the analyzed samples. The counting efficiency is about 40% and the lower limit of the procedure, with 95% confidence, is 7 mBq/sample for 1000 minute counting time.24 The details of the analytical steps are given in Fig. 2.

*Alpha-spectrometry:* The dried sample (1–2 g) is spiked, for chemical recovery and activity calculation, with about 80 mBq <sup>208</sup>Po and dissolved using mineral acids  $(HNO<sub>3</sub>, HF and HCI)$ . Finally the sample residuals is dissolved in about 30 ml 0.5M HCl. The sample is heated to 85 °C and about 100 mg of ascorbic acid is added to the hot solution to reduce the iron Fe(III) to Fe(II). Then, polonium isotopes are auto-deposited from the solution at temperatures between 80–90 °C onto rotating, clean mirror finishing, stainless steel disk fixed in a Teflon disk holder.25,26 The plated disk is measured using an alpha-spectrometer (Canberra 4701 vacuum chamber) based on passivated implanted planar silicon (PIPS) detector with 450 mm2 surface area, about 25% counting efficiency and 20 keV resolution for  $^{241}$ Am alpha-energy at 5.48 MeV, and connected to a computerized multichannel analyzer (MCA) operating with Genie 2000 software (Canberra). The average chemical recovery is 75%, and the individual values ranged from 50 to 100%. The sample is measured for 1000 minutes, applying a lower limit of detection of 1 mBq, with  $95\%$  confidence.<sup>24</sup> The details of the analytical steps are given in Fig. 3.



*Fig. 1.* Decay chart of <sup>210</sup>Pb



*Fig. 2.* Flowchart of the radiochemical analysis of  $^{210}$ Bi ( $^{210}$ Pb) by beta-counting



*Fig. 3.* Flowchart of the radiochemical analysis of <sup>210</sup>Po (<sup>210</sup>Pb) by alpha-spectrometry

*Table 1.* Comparison of parameters of various analytical techniques for the determination of <sup>210</sup>Pb in environmental samples

Method	Gamma-ray spectrometry	Beta-counting	Alpha-spectrometry
Sample size, g	100		$1 - 3$
Counting time, minutes	1000	1000	1000
Sensitivity, $s^{-1}$ ·Bq <sup>-1</sup>	$2.9 \cdot 10^{-4}$	2.5	
Background, cpm	0.5	0.5	0.005
Counting efficiency, %		40	20
$MDA$ ,* mBq, in 1000 minutes	440	7.1	
Duration of complete analysis	1 day	$>10$ days	$3-6$ moths**

\* MDA: Minimum detectable activity.

\*\* 3 days, in the case of Pb–Po secular equilibrium existence.

## **Results and discussion**

Comparison of the main parameters of the three different analytical techniques, gamma-spectrometry, beta-counting and alpha-spectrometry is given in Table 1. They differ over a wide range of analyzed sample size and counting system background and minimum detectable activity (MDA). It is noticeable that alpha-spectrometry achieves the lowest MDA (1 mBq/sample), amongst the three analytical techniques, while the MDA for gamma-spectrometry is the highest amongst all three techniques. Concerning the duration of the 210Pb complete analysis (source preparation and measurement), it is ranged from one day for gamma-spectrometry to more than 10 days for betacounting. While for alpha-spectrometry, the complete analysis duration is at least three days for sample dissolution, alpha-source preparation and alphaspectrometry, and varied widely according to the time of sample dissolution that depends on sample type. Also, the time needed before starting sample analysis differs and depends on the used analytical techniques. Analysis of 210Pb using both gamma-spectrometry and betacounting is possible without time delay before starting

the analysis. For alpha-spectrometry, the time delay before analysis depends on 210Pb–210Po secular equilibrium condition in the sample. If the secular equilibrium is already existed, the samples could be analyzed without time delay. Otherwise, it is essential to first get rid of 210Po existed in the samples via either auto plating of 210Po on a stainless steel disk or sample ashing at  $600 \degree C$ .<sup>27</sup> Accordingly, <sup>210</sup>Po can be analyzed after 3–6 months delay. It should be mentioned that the ingrowth factor of  $^{210}P_0$  as a decay product of  $^{210}P_0$ during the storage time should be taken into consideration. Ideally, to be sure of reaching secular equilibrium, the sample should be stored at least for two years, especially for samples with expected higher <sup>210</sup>Po concentration than that of 210Pb.

Three aspects should be considered for evaluating the methods. (1) The attainable detection limit decides whether a method is successfully applicable at all for the investigations. (2) The duration of a complete analysis can exclude methods of longer duration if there is an urgent need for the results. (3) The total expenditure in work and equipment has to be considered if economic limitations are important.22 Based on these aspects one method is chosen for 210Pb routine measurements for the demanded investigation but as necessary measures of analytical quality assurance some selected samples should be measured using another analytical technique. To guarantee the comparability of the results from these different analytical methods, the advantages and disadvantages of each method and the sources of data discrepancies and errors should be cleared. In this work, it is planned to apply these aspects using 210Pb measurement results of some selected geological, processed geological, soil and sediment samples.

*Gamma-ray spectrometric analytical technique:* Its main advantages are being fast, nondestructive, relatively simple sample preparation with no need of preliminary chemical separation, and direct analysis without delaying time through the measurement of 46.5 keV gamma-energy transition. However, the main disadvantages are its relatively high MDA and the often difficult corrections for self-attenuation in the sample matrix.28–30 The relative high MDA of gammaspectrometry is due to both the low emission probability (4.05%) and low energy transition of gamma-line. For a given sample container volume and geometry, the selfattenuation can significantly vary from sample to sample because it depends strongly on both the composition and apparent density of the sample.29 Self-attenuation can be theoretically calculated using physical models of interaction between gamma-rays and matter, computed with a Monte Carlo technique. Alternatively, some experimental approaches have been proposed and mentioned by PILLEYRE et al.<sup>19</sup> One approach dealt with the determination of absolute activity of large volume geological samples, without being hindered by selfattenuation. It was based on replicate counting of increasing volumes of the unknown samples. Good results were obtained but it was time consuming. Another approach have reported a method based on an evaluation of the transmission of low-energy gammarays from a 210Pb point source placed on an aluminum container in the presence and absence of the sample. In addition, others attempted to establish a direct correspondence between the measured count rate for the sample and the count rate expected for material identical to that used for efficiency calibration using gamma-ray transmission, this was for measuring  $241$ Am (at 59.6 keV), where the situation is nearly the same as for 210Pb.19

*Beta-particle counting of 210Bi technique:* The main advantage is the relatively low limit of detection, in the range of several mBq per sample. The main disadvantages are being destructive, the need of radiochemical separation and beta-particle source preparation, the need of waiting 10–30 days in order to count the prepared source and indirect measurement of 210Pb in the analyzed samples. There are different analytical methods for lead separation such as ionexchange method with EIChrome Sr. Spec. resin or

Dowex 1x8 resin, and solvent extraction methods with diethyl dithiocarbanic acid (DDTC) or trioctylamin/toluene. The lead reagent, which is used as a yield tracer (carrier), could be a source of error.  $CLAYTON<sup>17</sup>$  had analyzed a sample of lead of Tudor origin (virgin) and modern commercial reagent grade lead nitrate and the specific activity of  $210Pb-210P<sub>0</sub>$  were  $10.9\pm0.7$  and  $500\pm40$  Bq/kg lead respectively.<sup>19</sup> The specific activity of <sup>210</sup>Pb<sup>-210</sup>Po in the lead nitrate, which used in our analysis, is 18.2±2.3 Bq/kg  $(29.1\pm3.7 \text{ Bq/kg}$  lead), as shown in Table 5.

*Alpha-spectrometry of 210Po technique:* The main advantages are the excellent low limit of detection (in the range of few mBq per sample), the selectivity of polonium plating onto the stainless steel disk and the relatively less chemical preparation steps compared to that is associated with beta-counting. Waiting time required to achieve the analysis, being destructive and the need for careful chemical treatment are considered as the main disadvantages of this technique. $31,32$ 

Specific activity of  $^{210}Pb$  (Bq/kg) in geological, processed (geological samples have been exposed to some physical and chemical processing) and soil, and sediment samples, and their average are given in Tables 2, 3 and 4 respectively and shown in Fig. 4. The relationships and data correlations of 210Pb specific activity that were measured using three different analytical techniques (gamma-spectrometry, betacounting and alpha-spectrometry) in all samples and in each sample type (i.e., geological, processed, soil and sediment) are shown in Figs 5 and 6, respectively.

For geological samples, the existence of some discrepancies (but not vivid) in the results of some samples (specially the geological and processed samples) obtained from the different techniques was noticed. On the contrary, soil samples results showed acceptable concurrence amongst the different techniques. For sediment samples, the 210Pb specific activity measured using gamma-spectrometry and alphaspectrometry has trend of comparability of the results, although some samples has a higher concentration of 210Pb using one technique more than the other, without the existence of clear trends, as shown in Fig. 4. Generally, the average specific activity of <sup>210</sup>Pb in each sample type for each analytical technique and its over all average (for all samples of the same type and all analytical techniques) are mostly comparable and within the error values, as shown in Fig. 4. It is obvious that the specific activity of 210Pb measured using alphaspectrometry of  $210P<sub>Po</sub>$  is slightly higher than that was measured by gamma-spectrometry and could be explained by the sample self-attenuation. The sample self-attenuation correction has not been applied for our gamma-measurements. The results obtained for all samples by the different techniques (Fig. 5), are strongly correlated with correlation coefficients  $(R^2)$  very close to unity. The difference between the data linear fitting and the dashed line, represents the assumed identical results, is clear especially for highly active samples (geological and processed samples) where the alpha-spectrometry results seemed higher than that obtained by gammaspectrometry. These differences could be explained by the expected self attenuation in some samples.

Accordingly, careful efficiency calibration should be carried out to elude this problem. On the other hand, another issue concerning self attenuation problem should be considered, where empirical and experimental methods could be used to take the self attenuation in the lower energies region into consideration. $21,29$ 

*Table 2.* Specific activity of 210Pb (in Bq/kg) in geological, processed and soil samples using various analytical techniques

Method	Gamma-spectrometry				Beta-counting			Alpha-spectrometry
Sample	$A^*$ $\pm$	$E^{**}$	A	土	E	A	土	E
$G1+$	279.0 $_{\pm}$	5.6	251.3	$^{+}$	2.7	396.3	土	12.6
G <sub>2</sub>	34.8 $\pm$	3.8	43.0	$_{\pm}$	0.9	36.5	$^{+}$	2.4
G <sub>3</sub>	64.9 $\pm$	5.3	65.2	$^{+}$	1.0	85.3	土	4.3
$P1^{++}$	251.0 $\pm$	14.8	216.1	$^{+}$	1.9	355.9	$\pm$	10.7
P <sub>2</sub>	154.0 $^{+}$	6.9	277.4	$\pm$	3.3	236.9	土	11.4
P <sub>3</sub>	202.0 $_{\pm}$	14.1	290.1	$^{+}$	2.8	300.6	$_{\pm}$	8.6
P 4	173.0 $_{\pm}$	17.3	116.7	$^{+}$	1.3	234.2	土	7.2
$S1^{++}$	19.8 土	5.8	14.0	$\ddot{}$	0.7	19.1	$^{+}$	1.1
S <sub>2</sub>	20.7 土	5.2	17.4	$\pm$	0.6	23.6	土	1.3
S <sub>3</sub>	15.1 $\pm$	0.8	15.1	$\pm$	0.8	19.2	土	1.0
S <sub>4</sub>	25.4 $\pm$	4.8	18.3	$^{+}$	0.8	21.1	$^{+}$	0.9
S <sub>5</sub>	31.6 土	5.1	17.2	$^{+}$	0.7	21.3	土	1.1

\* Specific activity, Bq/kg.

\*\* Error (statistical and counting error only).

<sup>+</sup> Geological sample.

++ Processed sample (physical treated geological samples).

+++ Soil sample.

Sample No.	$210Pb*$	$\pm$	$E^*$	$^{210}Pb***$	$\pm$	E
$\mathbf{1}$	29.34	$\pm$	3.4	73.35	$\pm$	3.4
$\overline{\mathbf{c}}$	13.95	$\pm$	1.37	18.78	$\pm$	1.2
$\overline{3}$	80.99	Ŧ	3.13	96.01	$\pm$	5.7
$\overline{4}$	9.88	$\pm$	1.02	15.71	$\pm$	0.8
5	19.5	士	1.94	16.09	土	1.3
6	24.5	$_{\pm}$	5.6	28.8	土	2.1
7	11.08	$\pm$	0.98	17.97	$\pm$	1.3
8	13.54	$\pm$	1.42	14.49	$\pm$	1.2
9	21.1	士	7.0	25.2	$\pm$	2.5
10	14.07	$\pm$	1.22	14.83	$\pm$	1.2
11	7.9	$\pm$	0.79	8.07	$\pm$	0.7
12	25.61	士	2.59	31.61	土	4.7
13	7.08	$\pm$	0.9	12.38	土	1.3
14	22.05	士	3.58	17.54	土	1.3
15	23.71	Ŧ	3	17	土	1.6
16	81.75	Ŧ	5.1	81.41	土	4.3
17	14.63	$\pm$	1.5	14.51	$\pm$	0.9
18	29.63	$\pm$	$\overline{c}$	32.68	$\pm$	1.7
19	8.72	$\pm$	1.1	12.29	土	1.4
20	24.8	$_{\pm}$	6.7	33	土	3.2
21	16.93	士	1.8	22.04	$\pm$	1.9
22	14.82	$\pm$	1.8	23.26	$\pm$	1.1
23	22.1	士	5.1	24.7	土	2.4
24	29.63	土	3.3	34.75	土	2.6
25	9.44	士	0.8	13.86	$\pm$	1.1
26	19.76	土	2.2	25.42	土	2.9
27	11.4	士	1.4	23.31	土	2.4
28	23.71	$\pm$	2.6	13.39	$\pm$	1.5

*Table 3*. Specific activity of <sup>210</sup>Pb (in Bq/kg) in sediment samples using gamma-ray and alpha-spectrometry techniques

\* Statistical and counting error only.

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Sample type	Gamma-spectrometry	Beta-counting	Alpha-spectrometry	Average
Geological	$126.2 \pm 76.9, 133.2*$	$119.8 \pm 66.0$ , 114.4	$172.0 \pm 112.7$ , 195.2	$139.6 \pm 16.7, 28.9$
	$(34.8 - 279.0)$ [3] +	$(43.0 - 251.3)$ [3]	$(36.5 - 396.3)$ [3]	$(119.8 - 172.7)$ [3]
Processed geological	$195.0 \pm 21.1, 42.3$	$225.1 \pm 39.6, 79.2$	$281.9 \pm 29.1, 58.1$	$234.2 \pm 25.4, 44.1$
	$(154.0 - 251.0)$ [4]	$(116.7-290.1)$ [4]	$(234.2 - 355.9)$ [4]	$(195.0 - 281.9)$ [4]
Soil	$22.5 \pm 2.8, 6.3$	$16.4 \pm 0.8$ , 1.8	$20.9 \pm 0.8$ , 1.8	$19.9 \pm 1.8$ , 3.2
	$(15.1 - 31.6)$ [5]	$(14.0 - 18.3)$ [5]	$(19.1 - 23.6)$ [5]	$(16.4 - 22.5)$ [5]
Sediment	$22.7 \pm 3.4, 18.0$		$27.2 \pm 4.0, 21.3$	$24.9 \pm 2.3, 3.2$
	$(7.1 - 81.8)$ [28]		$(8.1 - 96.0)$ [28]	$(22.7 - 27.2)$ [28]

*Table 4.* Average specific activity of <sup>210</sup>Pb (in Bq/kg) in environmental samples using various analytical techniques

\* Average ± standard error, standard deviation.

+ (range) [number of samples].



*Fig. 4.* Specific activity of <sup>210</sup>Pb in environmental samples (geological, processed geological, soil and sediment) using gamma-spectrometry, beta-counting and alpha-spectrometry



*Fig. 5.* Correlations between the specific activity of <sup>210</sup>Pb in environmental samples measured by various analytical techniques

*Table 5.* Comparison of the specific activity of <sup>210</sup>Pb (in Bq/kg) in some selected reference material samples using gamma- and alpha-spectrometry and their reference values

Sample	Gamma-spectrometry $A* + E**$	Alpha-spectrometry $A \pm E$	Reference value
IAEA-384, sediment $(1)^{k}$	$23.5 \pm 1.3$		$23.5(22.2 - 24.2)$
IAEA-326, soil $(4)$	$43.4 \pm 6.7$	$43.14 \pm 2.02$	$52.5(47.9 - 57.1)$
IAEA-327, soil $(2)$		$51.8 \pm 4.8$	58.8 (53.9–63.7)
IAEA-135, marine sediment (2)	$50.61 \pm 7.58$		$48(42.2 - 54.1) +$
IAEA-RGU, uranium ore (2)		$5092 \pm 283$	4914 (4844-4984)
Lead nitrate, $Pb(NO_3)_{2}++$ , Analytical grade (2)		$18.17 \pm 2.32$	

\* Specific activity, Bq/kg.

\*\* Error (statistical and counting error only).

+ Information value.

++ Used as carrier.

& Number of analysis.



*Fig. 6.* Correlations between the specific activity of <sup>210</sup>Pb in various environmental samples measured by various analytical techniques

The specific activity of  $210Pb$  in each sample type using three analytical techniques is shown in Fig. 6. The correlation coefficient between gamma- and alphaspectrometry measurements are stronger than that between gamma-spectrometry and beta-counting measurements. These discrepancies are very clear for soil samples without any clear reason. It is well known that gamma-spectrometry measurements are performed using bulk amounts of samples, so, the homogeneity issue does not bother the analysts. On the other hand, regardless of their good MDA, both alpha- and betaspectrometry techniques are performed based on a relatively smaller sample size. So, this might brings up the homogeneity problem.

Regarding the geological and processed geological samples, the discrepancies in the results among the three techniques could be explained by the lack of sample homogeneity and the existence of hot spots. This could be more clear in the case of the processed samples since they are both physically and chemically (washed) treated.

Twenty eight sediment samples were analyzed using two different techniques (gamma- and alphaspectrometry) are given in Table 3 and shown in Fig. 4.



*Fig. 7.* Specific activity of <sup>210</sup>Pb in some selected reference samples with their reference values using various analytical techniques

The correlation coefficient was calculated for these the two sets of results and was 0.9. Some samples showed good agreement for both techniques (samples 8, 10 11, 16, 17 and 18), (Figs 5 and 6). However, other samples showed distinct discrepancies. The homogeneity problem may be a major factor, in addition to the necessity of sample self attenuation correction that was not corrected in all of our results.

The specific activity of  $210Pb$  in some selected reference materials using gamma- and alphaspectrometry techniques are given in Table 5 and shown in Fig. 7. The results are showing good accuracy for both techniques compared to the given reference values. One reference sample was analyzed using both techniques and they gave a spectacular agreement, though relatively lower than the reference value but it falls within the reference range. It should be mentioned that the IAEA reference samples often follow a tedious procedure of mixing and strict homogeneity tests prior to releasing to laboratories for use as reference materials. So, these results are considered supportive of our point of view regarding the homogeneity issue.

#### **Conclusions**

For 210Pb analysis in environmental samples, the three analytical techniques give comparable results for the same sample set. For routine analysis, the used analytical technique should be chosen carefully based on advantage and disadvantage of the each technique, and the analysis requirements. Gamma-spectrometry is easier, needs less man-power and cost than the other techniques. Best is the direct measurement of  $210Pb$  in a relatively large volume sample with no waiting time before analysis and minor effect of sample inhomogeneity problem. Its major advantages are its relatively high minimum detectable activity (MDA), about 0.44 Bq/sample, and the necessity to correct the counting efficiency for the gamma-ray attenuation due to sample matrix and composition.

Beta-counting needs tedious chemical work and waiting time  $(2-3$  weeks) before measurement for  $2^{10}$ Bi build up in the sample source, but no waiting time needed before sample analysis. Its MDA (0.007 Bq/sample) is much lower than that of gammatechnique. So it is considered moderate regarding the time consumption.

Alpha-spectrometry needs relatively simple chemical sample treatment and source preparation and no waiting time before measurement. It needs also to ensure a certain degree of equilibrium between 210Pb and its grand-daughter  $^{210}P_0$ , which requires waiting for 3–6 months after the first <sup>210</sup>Po analysis or two years especially for the sample with an expected enrichment of  $^{210}$ Po to  $^{210}$ Pb. Its MDA (0.001 Bq/sample) is the lowest amongst the three techniques. On the other hand, using a relatively small size of the sample for beta-counting and alpha-spectrometry analytical techniques could increase the analytical error due to the possible lack of sample homogeneity. Therefore, it is recommended for the analysts to determine exactly their needs and to know a little about the samples history to be able to decide on the best analytical technique to use for each specific sample or set of samples. For instance, if the analyst is given a sample with expected high 210Pb specific activity sample, gamma-spectrometry is strongly

recommended. On the other hand if the samples are expected to have a relatively low 210Pb specific activity, either alpha-spectrometry or beta-counting are recommended. The choice between the alphaspectrometry and beta-counting could be decided based on the accuracy needed and the time limits for the analyst.

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