EVALUATION OF METHODS FOR THE DETERMINATION OF $^{210}$Pb AND $^{210}$Po IN CA-RICH ASH SAMPLES

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Nuclear techniques and measurement methods are widely used for environmental monitoring and research using natural and artificial radionuclides as indicators for atmospheric, terrestrial and marine transport processes.
The natural radionuclide,

$t_{1/2} = 138.38$ days,

Alpha particle emitter.
The natural radionuclide,
\[ t_{1/2} = 22.3 \text{ years}, \]
\[ \text{Beta} \ (E_{\text{max}} = 0.018 \text{ MeV}) \text{ and gamma} \ (E_{\gamma} = 0.047 \text{ MeV}) \text{ emitter.} \]
- Fossil fuel burning power plant,
- Fertilizer industries,
- Nuclear weapons and,
- Exhaust gasses of traffic.

- Volcanic activities,
- Forest fires.
Radiochemical Procedure for $^{210}\text{Pb}$

There are three alternative methods of analysing the total activity of $^{210}\text{Pb}$ in a sample:

- Alpha spectrometry
- Beta spectrometry
- Gamma spectrometry
\(^{210}\text{Pb}\) concentration can be indirectly determined by alpha-ray spectrometry through its decay progeny \(^{210}\text{Po}\).
Sample preparation must convert the raw sample into a form that is suitable for alpha spectrometry. This implies two requirements for the preparation:

- Produce a thin sample,
- Chemically separate elements that would produce chemical or radiochemical interferences.
Tracers (²⁰⁸Po or ²⁰⁹Po) are added at the start of the analysis.

The samples are analysed by radiometric methods as indicated in Figure.

Polonium is spontaneously plated on a copper or silver discs.
After the first deposition of $^{210}$Po, the solution is kept for one year to allow $^{210}$Po ingrowth from the $^{210}$Pb contained in the solution.

The samples are then re-plated and the $^{210}$Po activities determined.

Parent and daughter activities for compound decay with secular equilibrium

$$A_{total}^{(210 \text{Po})} = A^{(210 \text{Po})}[^{210} \text{Pb}] + A^{(210 \text{Po})}$$
The second deposition of $^{210}\text{Po}$ provided information on the $^{210}\text{Pb}$ content of the samples, and also on the extent to which the initial $^{210}\text{Po}$ is supported by its $^{210}\text{Pb}$ grandparent.

After attaining the radioactive equilibrium $^{210}\text{Pb}$ (precursor of $^{210}\text{Po}$) concentrations are determined from $^{210}\text{Po}$ activities measured through its 5.30 MeV alpha particle emission.
Gamma Spectrometer

$^{210}\text{Pb}$ can be measured by gamma spectrometry using a high-purity germanium (HPGe) detector.
Liquid Scintillation Counting (LSC) represents a suitable alternative to other spectrometric techniques for direct determination of $^{210}$Pb activity through its beta energy line at 63.5 keV.
Starting point

To elucidate the applicability of the proposed methods for determination of the activity concentrations of $^{210}\text{Pb}$ and $^{210}\text{Po}$ in Ca-rich ash samples by LSC.
The separation method of $^{210}$Po and $^{210}$Pb has been modified for ash samples, which were collected from oil-shale power plant in Estonia.
The method was applied to IAEA/RGU-1, IAEA-444 soil certified reference material and Ca-rich ash samples.
<table>
<thead>
<tr>
<th>Mass of sample (g)</th>
<th>Acid (mL)</th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HNO₃</td>
<td>HF</td>
<td>HCl</td>
</tr>
<tr>
<td>0.50</td>
<td>14</td>
<td>2</td>
<td>–</td>
</tr>
<tr>
<td>0.50</td>
<td>15</td>
<td>1</td>
<td>–</td>
</tr>
<tr>
<td>0.50</td>
<td>14.5</td>
<td>1.5</td>
<td>–</td>
</tr>
<tr>
<td>0.50</td>
<td>15.5</td>
<td>0.5</td>
<td>–</td>
</tr>
<tr>
<td>0.50</td>
<td>3.5</td>
<td>2</td>
<td>10.5</td>
</tr>
<tr>
<td>0.50</td>
<td>4</td>
<td>1</td>
<td>11</td>
</tr>
<tr>
<td>0.50</td>
<td>4</td>
<td>–</td>
<td>12</td>
</tr>
<tr>
<td>1.00</td>
<td>21.5</td>
<td>3.5</td>
<td>–</td>
</tr>
<tr>
<td>1.00</td>
<td>21</td>
<td>4</td>
<td>–</td>
</tr>
<tr>
<td>1.00</td>
<td>20</td>
<td>5</td>
<td>–</td>
</tr>
</tbody>
</table>
- Temperature limitation,
- High acid consumption,
- Unsatisfactory digestion quality,
- Contamination risk and,
- Digestion duration.

Best results were obtained by a digestion method with mixture of nitric acid and hydrofluoric acid for Ca-rich ash samples.
After determining the suitable sample mass, additional experiments were done to test the effect of different mixture ratios of HNO$_3$ and HF on the dissolution of samples.

It’s sufficient to add 2 mL of HF acid to 0.5 g ash sample for the decomposition of silicates.
HF reacts with calcium to form inert calcium fluoride (CaF$_2$).

Boric acid in H$_2$O (saturated solution) was used in order to dissolve CaF$_2$ precipitation and to remove the remaining HF from the sample solution.
use 0.5 g ash samples, digest them by a mixture of HNO₃ and HF, add 15 mL of saturated boric acid.

Heating conditions for microwave digestion system

<table>
<thead>
<tr>
<th>Step</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>150</td>
<td>170</td>
<td>180</td>
<td>0</td>
</tr>
<tr>
<td>Ramp (min)</td>
<td>0</td>
<td>5</td>
<td>0</td>
<td>15</td>
</tr>
<tr>
<td>Hold time (min)</td>
<td>5</td>
<td>10</td>
<td>15</td>
<td>20</td>
</tr>
</tbody>
</table>
Sr-resin column was prepared for the separation of $^{210}\text{Po}$, $^{210}\text{Bi}$ and $^{210}\text{Pb}$ from a sample solution.
\(^{210}\)Po concentrations in discarded solutions were measured by LSC to check the effect of column dimensions.

Elution spectrum for \(^{210}\)Po discarded sample
Quantulus 1220 (PerkinElmer) liquid scintillation counter

The optimum PSA (pulse shape analyser) level was set to “10” for $^{210}$Po, “100” for $^{210}$Pb measurements.
All cocktails demonstrated high counting efficiency for $^{209}$Po spiked solutions.

Optiphase HiSafe 3 was chosen as an optimal liquid scintillation cocktail.
MINITAB Statistical software was used to evaluate the parallel samples.

The coefficient of variation (CV) of the samples with low activity is more than three times greater than that of the samples with high activity.

<table>
<thead>
<tr>
<th></th>
<th>$\bar{X}$</th>
<th>Standard deviation</th>
<th>Coefficient of variation (%)</th>
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<tbody>
<tr>
<td><strong>Low activity samples</strong></td>
<td>42.97</td>
<td>10.95</td>
<td>25.47</td>
</tr>
<tr>
<td><strong>High activity samples</strong></td>
<td>80.80</td>
<td>6.70</td>
<td>8.29</td>
</tr>
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</table>
Chi square goodness of fit test was used to compare the results for the low and high levels of activity measurements.

**low-level of parallel samples**
- \( x^2 = 11.154, \ P < 0.05 \)

**high-level of parallel samples**
- \( x^2 = 2.219, \ P > 0.05 \)
The chemical recovery of the procedure for $^{210}$Po ranged from 71 – 87% in RGU-1 and 34 – 61% in IAEA-444.
The main advantage of the method is the possibility to separate and measure $^{210}\text{Pb}$, $^{210}\text{Bi}$ and $^{210}\text{Po}$ originating from the same sample using Sr-resin column and LSC,

And do not have to wait for the secular equilibrium between $^{210}\text{Pb}$ and $^{210}\text{Po}$. 
The results have been discussed in terms of the suitability and repeatability for **high** and **low** activities of reference materials, and Ca-rich ash samples. **Determination of** $^{210}$Po **can be measured by LSC for high activity samples.**