



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

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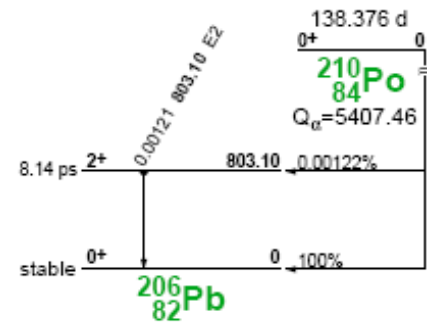
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☢ Nuclear techniques and measurement methods are widely used for environmental monitoring and research using natural and artificial radionuclides as indicators for atmospheric, terrestrial and marine transport processes.



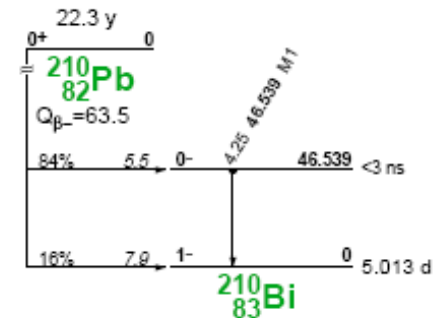
# 210Po

- ❖ The natural radionuclide,
- ❖  $t_{1/2}=138.38$  days,
- ❖ Alpha particle emitter.





- ❖ The natural radionuclide,
- ❖  $t_{1/2}=22.3$  years,
- ❖ Beta ( $E_{\max}=0.018$  MeV) and gamma ( $E_{\gamma}=0.047$  MeV) emitter.



*[Table of Isotopes CD ROM Edition; Richard B. Firestone; Wiley-Interscience]*

- ❖ 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 for Alpha Spectrometry

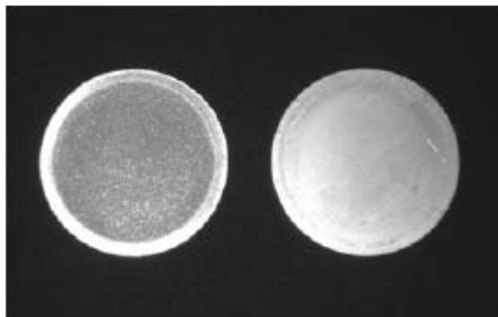
Sample preparation must convert the raw sample into a form that is suitable for alpha spectrometry. This implies two requirements for the preparation:

- 🍷 Produce a thin sample,
- 🍷 Chemically separate elements that would produce chemical or radiochemical interferences.

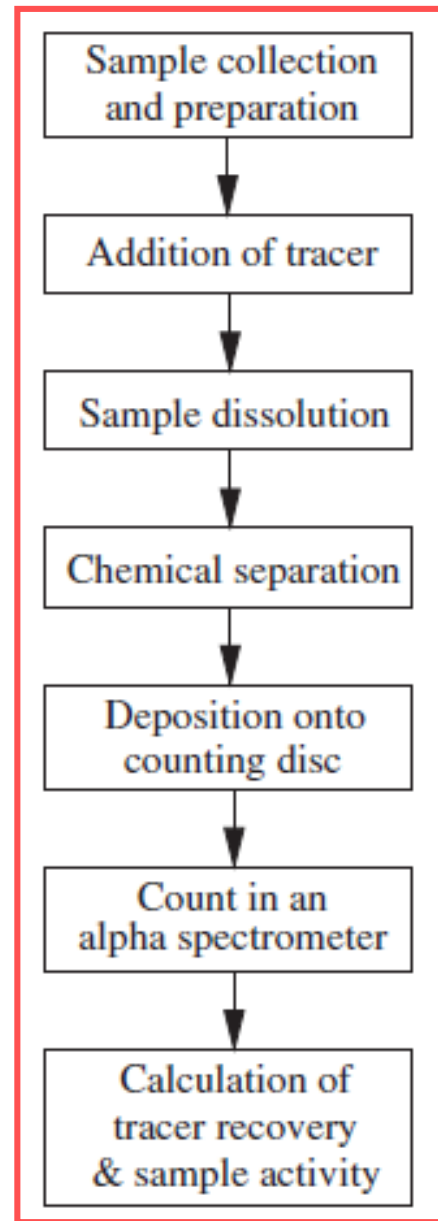




- ❖ Tracers ( $^{208}\text{Po}$  or  $^{209}\text{Po}$ ) are added at the start of the analysis.
- ❖ The samples are analysed by radiometric methods as indicated in Figure.
- ❖ Polonium is spontaneously plated on a copper or silver discs.

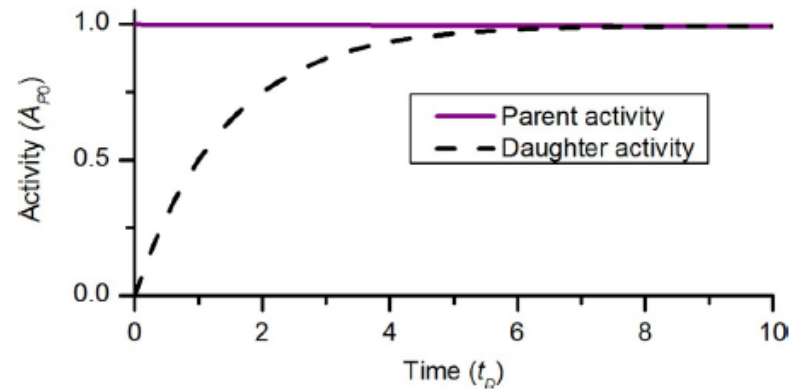


Nickel (l) and silver (r) discs after spontaneous deposition of polonium



✿ After the first deposition of  $^{210}\text{Po}$ , the solution is kept for one year to allow  $^{210}\text{Po}$  in-growth from the  $^{210}\text{Pb}$  contained in the solution.

✿ The samples are then re-plated and the  $^{210}\text{Po}$  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.



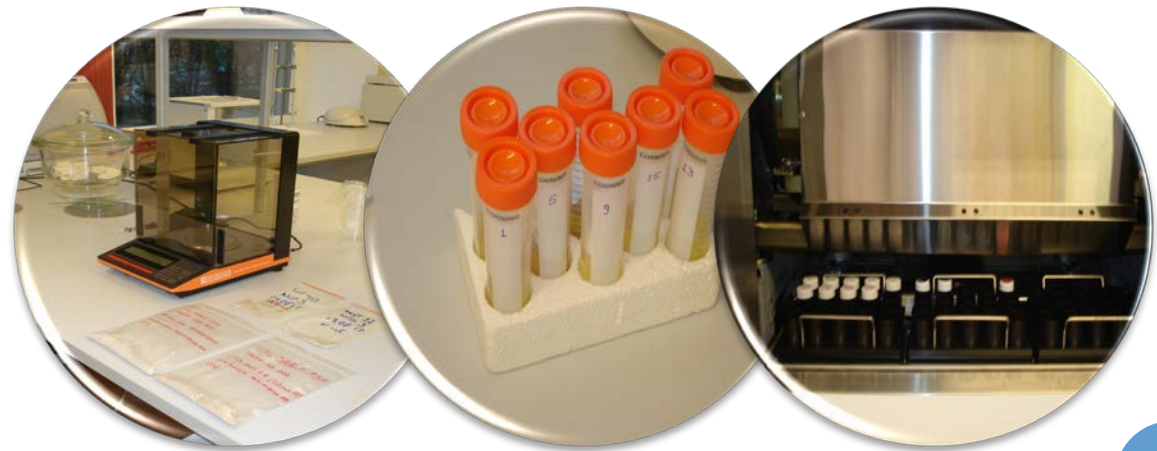


❁ Liquid Scintillation Counting (LSC) represents a suitable alternative to other spectrometric techniques for direct determination of  $^{210}\text{Pb}$  activity through its beta energy line at 63.5 keV.

# 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.





# Analysis

☢ The separation method of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  has been modified for ash samples, which were collected from oil-shale power plant in Estonia.





# Analysis

☢ The method was applied to IAEA/RGU-1, IAEA-444 soil certified reference material and Ca-rich ash samples.





Mass of sample (g)	Acid (mL)		
	HNO <sub>3</sub>	HF	HCl
0.50	14	2	–
0.50	15	1	–
0.50	14.5	1.5	–
0.50	15.5	0.5	–
0.50	3.5	2	10.5
0.50	4	1	11
0.50	4	–	12
1.00	21.5	3.5	–
1.00	21	4	–
1.00	20	5	–

- ❖ Temperature limitation,
- ❖ High acid consumption,
- ❖ Unsatisfactory digestion quality,
- ❖ Contamination risk and,
- ❖ Digestion duration.



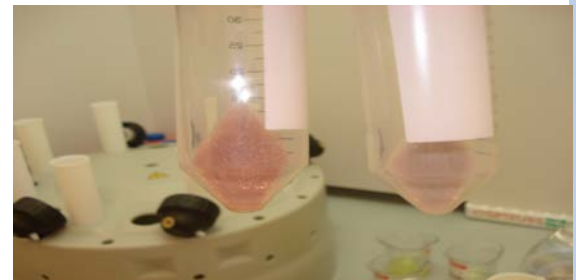
- ❖ Best results were obtained by a digestion method with mixture of nitric acid and hydrofluoric acid for Ca-rich ash samples.

❖ After determining the suitable sample mass, additional experiments were done to test the effect of different mixture ratios of  $\text{HNO}_3$  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.



The amount of HF



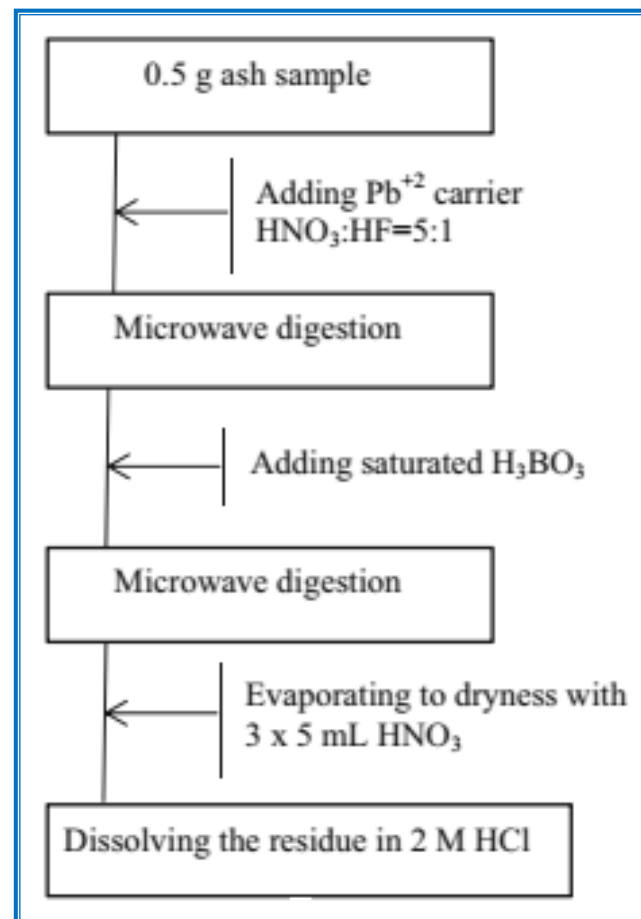
- ❖ HF reacts with calcium to form inert calcium fluoride ( $\text{CaF}_2$ ).
- ❖ Boric acid in  $\text{H}_2\text{O}$  (saturated solution) was used in order to dissolve  $\text{CaF}_2$  precipitation and to remove the remaining HF from the sample solution.



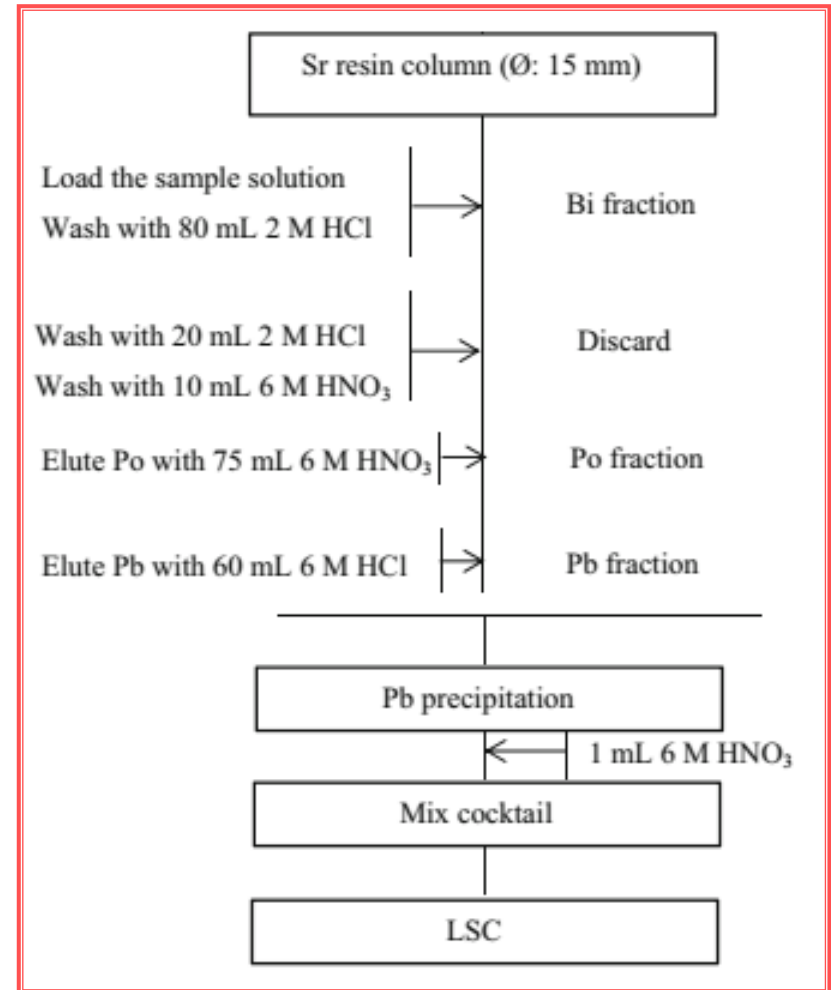
- ☢ use 0.5 g ash samples,
- ☢ digest them by a mixture of  $\text{HNO}_3$  and  $\text{HF}$ ,
- ☢ add 15 mL of saturated boric acid .

### Heating conditions for microwave digestion system

Step	1	2	3	4
Temperature (°C)	150	170	180	0
Ramp (min)	0	5	0	15
Hold time (min)	5	10	15	20

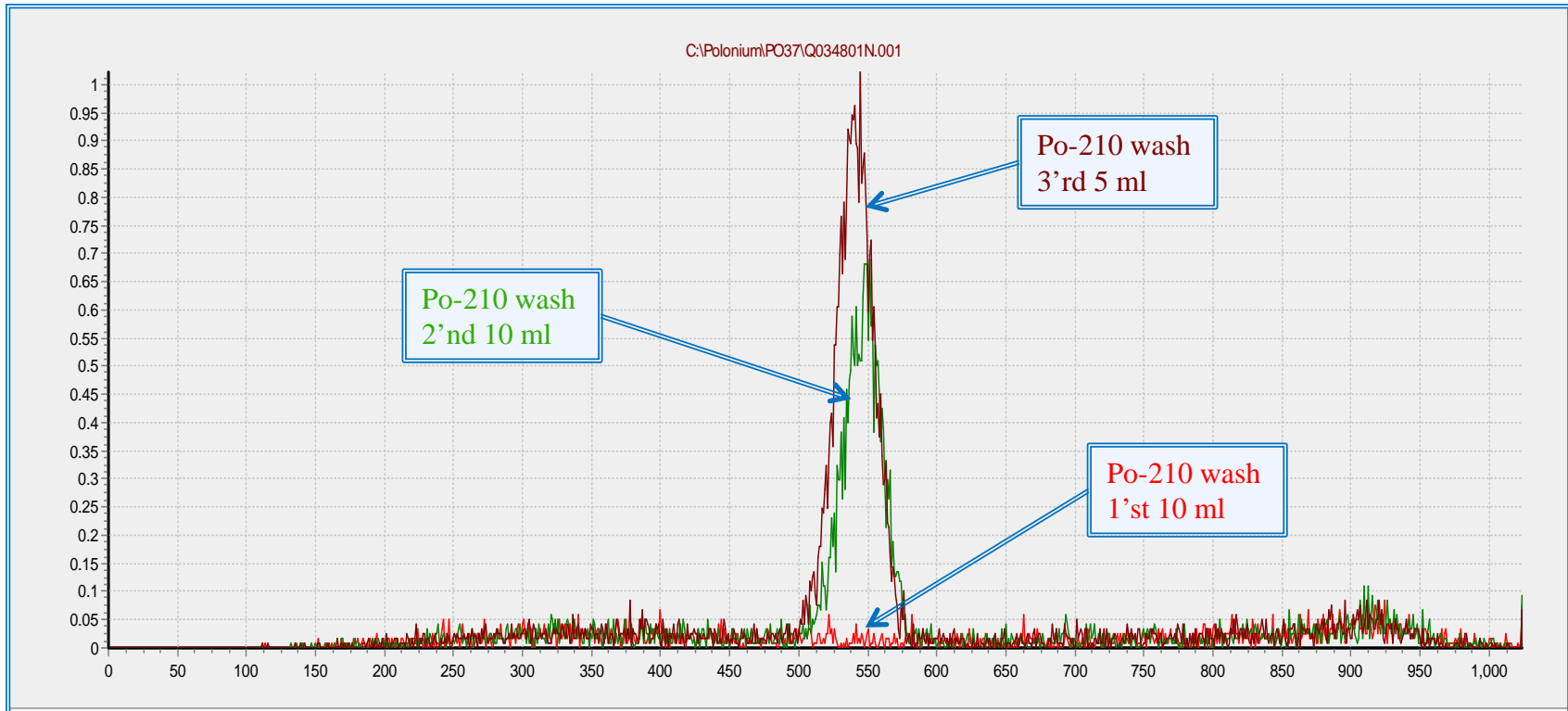


☢ Sr-resin column was prepared for the separation of  $^{210}\text{Po}$ ,  $^{210}\text{Bi}$  and  $^{210}\text{Pb}$  from a sample solution.





☢  $^{210}\text{Po}$  concentrations in discarded solutions were measured by LSC to check the effect of column dimensions.



Elution spectrum for  $^{210}\text{Po}$   
discarded sample

☢ Quantulus 1220  
(PerkinElmer) liquid  
scintillation counter

☢ The optimum PSA  
(pulse shape analyser)  
level was set to “10” for  
 $^{210}\text{Po}$ , “100” for  $^{210}\text{Pb}$   
measurements.



Ultima  
Gold AB

Insta-Gel  
Plus

Optiphase  
HiSafe 3

☢ All cocktails demonstrated high counting efficiency for  $^{209}\text{Po}$  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.

	$\bar{X}$	Standard deviation	Coefficient of variation (%)
<b>Low activity samples</b>	42.97	10.95	25.47
<b>High activity samples</b>	80.80	6.70	8.29

❖ 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

•  $\chi^2 = 11.154, P < 0.05$

high-level of parallel samples

•  $\chi^2 = 2.219, P > 0.05$

The chemical recovery of the procedure for  $^{210}\text{Po}$  ranged



71 – 87% in RGU-1



34 – 61% in IAEA-444

# Conclusion

- ❖ 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  $^{210}\text{Po}$ .





# Conclusion



- ❖ 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  $^{210}\text{Po}$  can be measured by LSC for high activity samples.



