RiO5 METHOD (16)

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^{210}Pb — acid digestion — sediment samples

Determination of ^{210}Pb in sediment samples

Disclaimer

It is the responsibility of the analyst to follow established safety and health practices. Although each laboratory identified as the source has tested the methods, each user should perform an individual validation procedure.

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1 SCOPE

The concentration of ^{210}Pb is determined by alpha spectrometry through its granddaughter ^{210}Po, assuming radioactive equilibrium between the two radionuclides. An acid digestion of the sediment is carried out by using HNO_3 and HF, followed by another digestion using H_3BO_3 in order to eliminate salts formed during the first digestion.

After digestion, the resulting solution is transferred to a Teflon beaker and is evaporated to incipient dryness. Small amounts of concentrated HCl are added to dissolve the sample residuals and to ensure the elimination of HNO_3. Afterwards, samples are diluted to 50-100 ml 1M HCl and approximately 50-100 mg of ascorbic acid is added to reduce the iron Fe(III) to Fe(II) while heating at 80 ^oC.

Finally, polonium isotopes are auto-plated onto silver disks at 80 ^oC while stirring for 8 hours. After polonium deposition, Po isotopes emissions are measured by alpha spectrometry using Passivated Implanted Planar Silicon, PIPS detectors (CANBERRA, Mod. PD-450.18 A.M).

2 EQUIPMENT and CHEMICAL REAGENTS

2.1 Equipment

- Standard laboratory equipment
- Teflon beakers
- Analytical balance with an accuracy of ± 0.1 mg
- Hot plate with magnetic stirrer
- CEM Mars 6 Microwave Digestion system
- Alpha spectrometer equipped with Si semiconductor (PIPS) detectors

2.2 Tracers

- ^{209}Po (aprox 0.4 Bq)

2.3 Chemical reagents

- Nitric acid (HNO_3 70 % QP)
- Hydrofluoric acid (HF 40 % PA)
- Boric acid (H_3BO_3)
- Hydrochloric acid (HCl)
- Ascorbic acid

2.4 Solutions

- 4% H_3BO_3

Preparation of 4% boric acid solution: 40g per litre made up with Milli-Q water, and dissolve on stirring hotplate in a closed volumetric flask with a magnetic stirrer added. Start slowly at

140 rpm and increase to 740 rpm over approximately 1 hour at 30°C until transparent. This should be enough for 1.6 digestions.

- 1MHCL

32% HCl 1M HCl. Add 96 mL of 32% hydrochloric acid to about 600 mL of MQ water in a 1 litre measuring cylinder and make up to 1L.

3 PROCEDURE

3.1 Preparation for the Microwave Digestion

Prepare the following material in close proximity to the scale:

- Digestion liners
- Digestion racks
- Samples to be analyzed
- Spatula
- Micropipette (100-1000mL)

1. Prepare the analytical balance .
2. Place the liner on the balance plate, tare and remove to add sample.
3. Add between 150 - 300 mg of sample.
4. Record the weights of the samples.
5. Place the liners in the racks following the sample order e.g.: 1 – 8, 9 – 16, 17 – 40.

3.2 Maximum capacity of the liners

The min volume for the MARS 6 cavity is 10 mL of acid or 50 mL of water. For the MARSXpress vessels the maximum operation volume is 30 mL.

Table 3.4 MARS Microwave Synthesis System – Features of Parallel Pressure Rotors.

	HP-500+	XP-1500+	MARSXpress
Turntable	14 ×	12 ×	40 ×
Vessel volume	100 mL	100 mL	55 or 75 mL
Operation volume	max. 70 mL	max. 70 mL	max. 30 or 50 mL
Vessel material	PTFE-PFA	PTFE-TFM	PFA
Operation pressure	30 bar	100 bar	30 bar
Max. temp.	260 °C	300 °C	260 °C
Temp. measurement	fiber optic	fiber optic	IR

3.3 Addition of acids and pre-digestion

1. Prepare the pipette with 3 rinses of the ^{209}Po tracer solution.
    a. The amount of tracer solution to add is a function of the original activity of the tracer. Add tracer to each sample and record weights.
2. Move the racks containing the samples to the fume hood. Always wear the appropriate PPE (PVC apron, double nitrile gloves and safety glasses) and place the liners in the rack after adding the acids.
3. Add 9 mL of nitric acid (HNO_3 65 % QP) to each of the liners and 3 mL of Hydrofluoric acid (HF 40 % PA) to achieve full digestion of the sediment samples (nitric acid to oxidize any organic material present and hydrofluoric acid to attack silicates).
4. Wait a minimum of 15 min before capping the liners to predigest the sample and allow for fumes to escape.
5. Replace liner caps inside the fume-hood and twist closed with the provided tool. This last step will be done outside the fume hood but only after making sure that all the liners are well placed in the rack and closed.
6. Finally place the liners in their corresponding slots in the carousel. Always start by filling the inner circle, if not full, then balance in the outer circle. Always make sure the samples are in the correct order.

3.4 Digestion

Program the Microwave digester using the Classic Method Sediment 12, 24 or 40, depending on the amount of samples:

Vessels	Ramp	T	Power
1-12	15 min to 180 °C	25 min at 180 °C	600 W
12-24	15 min to 180 °C	25 min at 180 °C	800 W
24-40	15 min to 180 °C	25 min at 180 °C	1800 W

3.5 Neutralization of HF

1. When the microwave program has finished and the liners are cold, place them in the rack and bring it to the fume hood. Always wear the appropriate PPE (double gloves, apron and safety glasses) and open the vessels inside the fume hood, when the vessel contents are at room Temperature. Point the vent hole always towards the back of the fume hood.
2. Add 15 mL of 4% boric acid solution to the samples in liners and place them in the carousel again using the same procedure as previous.
3. Program the Microwave digester using the Classic Method Boric Acid 12, 24 or 40, depending on the amount of samples.

Vessels	Ramp	T	Power
1-12	20 min to 170 °C	15 min at 170 °C	600W
12-24	20 min to 170 °C	15 min at 170 °C	800 W
24-40	20 min to 170 °C	15 min at 170 °C	1800 W

3.6 Samples with a high content of organic matter

For samples with a high content in organic matter, the following methodology needs to be followed to achieve full digestion:

1. Add 10 mL of nitric acid (HNO_3 65 % QP) to each of the liners and 2 mL of hydrogen peroxide 30%. Program the Microwave digester using the Classic Method Carbon.

    a. Wait 30 min before capping the liners to predigest the sample and allow for fumes to escape.

    b. Add the hydrogen peroxide very slowly to prevent the samples from overflowing.

2. When the digestion is finished and the liners have cooled down, open the liners inside the fume hood with special care. Point the vent hole always towards the back of the fume hood.

3. Add 3 mL of HF to the samples and program the Microwave digester using the Classic Method Sediment 12, 24 or 40, depending on the amount of samples.

4. Finally add 15 mL of 4% boric acid solution to the samples in the liners and program the Microwave digester using the Classic Method Boric Acid 12, 24 or 40, depending on the amount of samples.

3.7 Evaporation and preparation of plating

3.7.1 Evaporation

1. Quantitatively transfer the contents of the liners to pre-labelled 100 mL Teflon beakers. Clean the walls of the liners using a squirt bottle containing 1M HCl. Place the beakers on the hotplate to evaporate at 70-80°C until dry.

    a. In the Teflon beakers it will normally take 6- 8 hours.

2. Once the samples on the beakers have evaporated, add 2-3 mL of hydrochloric acid (HCl) and evaporate to dryness. Repeat this step twice more to fully eliminate the nitrates.

3.7.2 Preparation of plating

1. To give volume to the sample and sink the silver discs, add 50-100 mL of 1M HCl and cover with a watch glass. Insert a magnetic stirrer, place onto the stirring hotplate and agitate over low heat until the solution is clear and all residues have dissolved.

2. Quantitatively transfer the solution and stirrer from each Teflon beaker to pre-labelled 150 mL glass beakers using a squirt bottle containing 1M HCl to clean the walls of the teflon beaker. Cover with a watch glass and place on the stirring hotplate to reach a temperature of 75-80°C. At this point, add a tiny amount of ascorbic acid to the sample until it is colorless and transparent (to prevent the iron is deposited on the silver platter).

    a. The ascorbic acid needs to be added when de solution is warm.

3.7.3 Plating

1. Prepare the silver-plating discs for each sample. Discs need to be labeled on the

repellent-coated side. Use a hammer and tack to make a hole on the outer edge of the disk from the non-coated side. Using pre-cut nylon line (approx. 30cm length), thread through the hole and use tape to secure the discs in the beaker. Ensure that the silver-plating disc is submerged at least 1 cm from the surface of the HCl solution, but not touching the bottom of the beaker or the magnetic stirrer.

2. Leave it gently stirring for 6-8 hours checking periodically that the plating side of the disc is shiny. If it turns yellow, remove the disc and add more ascorbic acid.

3. After plating is finished, rinse with Milli-Q and then ethanol to dry and remove discs from beaker by allowing hanging from the tape until dry. Cut from the nylon lines and place in the corresponding pre-labeled envelopes for analysis by alpha spectrometer.

4 REFERENCES

Masqué i Barri, P. (1999) Estudi del comportament del 210Pb i el 210Po en el Mar Catalanobalear i el seu ús com a radiotraçadors. PhD thesis, Universitat Autònoma de Barcelona.

5 FLOW CHART

SAMPLE
0.150 - 0,300 gr sediment

Tracer: ^{209}Po
90µL sol.6

REAGENTS:
9 mL of nitric acid and 3 mL of hydrofluoric acid

- PVC apron, PVC long gloves and safety glasses
- wait 15 mins before capping the liners

DIGESTION:
classic method sediment 12, 24 or 40

NEUTRALIZATION OF HF:
15mL of 4% boric acid solution / classic method boric acid 12, 24 or 40

EVAPORATION:
transfer to 100mL teflon beakers (pre-labelled) / evaporate at 70-80°C until dry

- it will normally take 8 hours

add 2-3 mL of hydrochloric acid / evaporate to dryness x 3 times

PREPARATION OF PLATING:
add 50-100 mL of 1M hydrochloric acid / agitate over low heat

- cover with a watchglass, insert magnetic stirrer
- until solution is clear and all residue dissolved

transfer to 150 mL glass beakers (pre-labelled)
stir and heat to 75-80°C / add a tiny amount of ascorbic acid

- cover with a watchglass, insert magnetic stirrer
- add the ascorbic acid when the solution is warm until the sample is colourless and transparent

PLATING:
submerge the pre-labelled silver plating discs
gently stir for 6-8 hours at a temperature of of 75-80°C

- submerge at least 1 cm from the surface, not touching bottom of the beaker or magnetic stirrer
- check periodically that the plating side of the disc is shiny
- If it turns yellow, remove the disc and add more ascorbic acid.

6 IMAGES

Image 1:

Samples ready in the liners to go into the CEM MARS microwave.

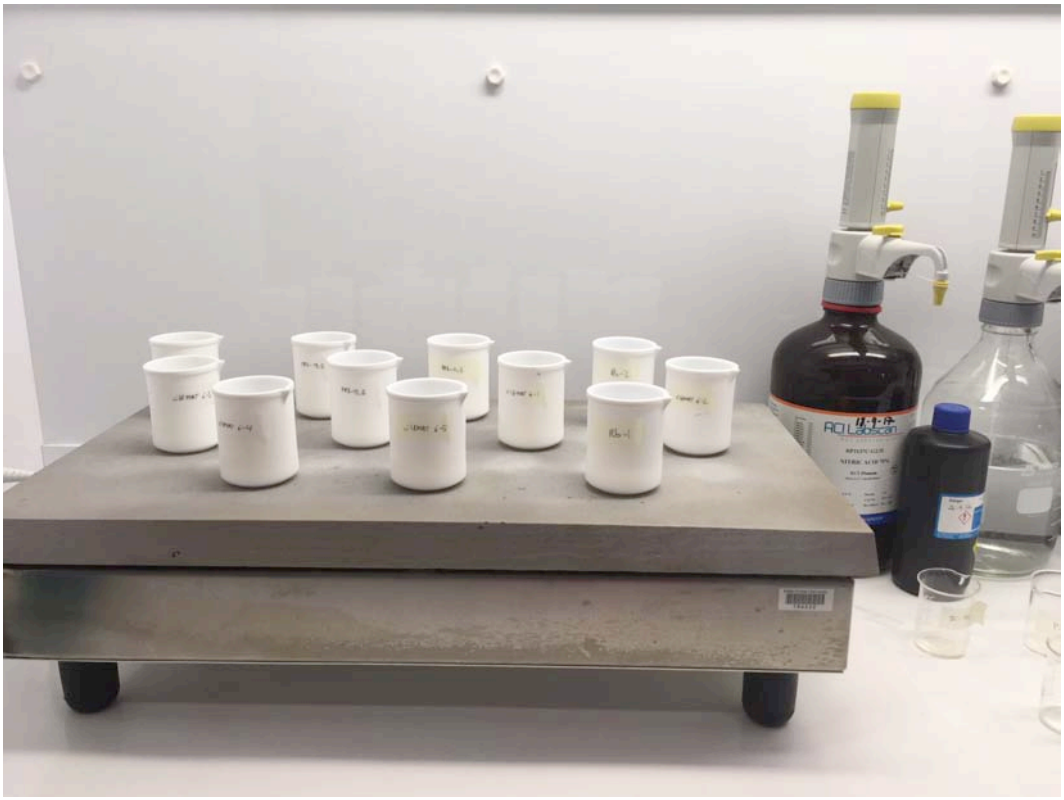
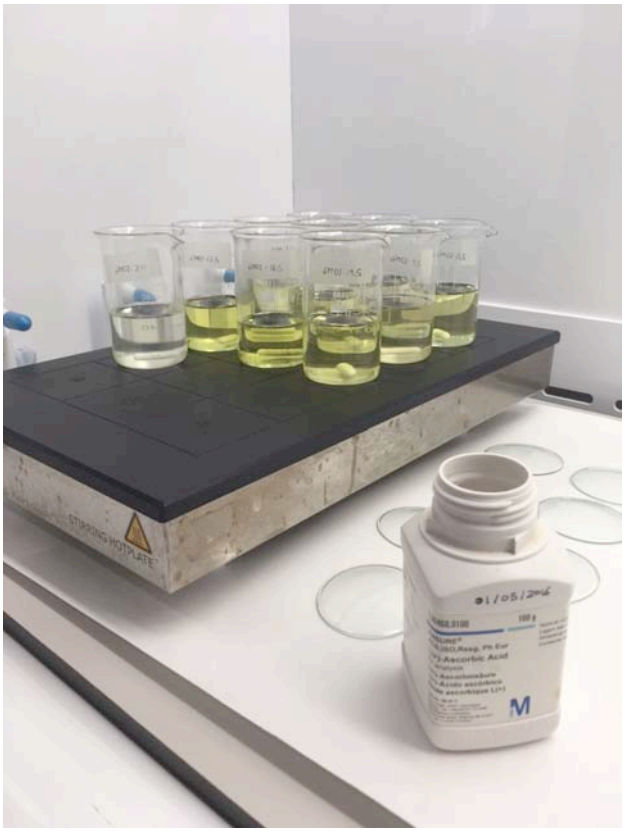


Image 2: Samples transferred to Teflon beakers and evaporating to dryness



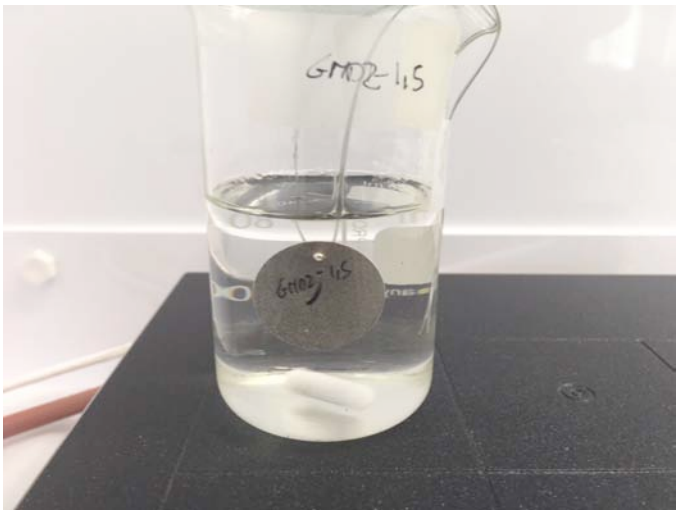


Image 3: Preparation of plating