RiO5 METHOD (20)

MEL-XMU

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^{210}Po and ^{210}Pb—Auto-plating —Seawater sample

Seawater sample preparation for polonium-210 and lead-210

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1 SCOPE

This method specifies the minimum requirements and laboratory methods for the analysis of ^{210}Po and ^{210}Pb in seawater samples with alpha-spectrometry.

Samples are collected in acid-cleaned container and co-precipitated with $Fe(OH)_3$ in the presence of Pb and ^{209}Po yield tracers. Po isotopes are auto-plated onto silver disks on board. Post processing take place in the land laboratory by separating residual Po from Pb and auto-plating ^{210}Pb-generated ^{210}Po. Po isotopes are measured by alpha-spectrometry. Corrections on ingrowth and decay are included in calculating the in situ ^{210}Po and ^{210}Pb activities (calculation see Rigaud et al., 2013).

2 EQUIPMENT CHEMICAL REAGENTS

2.1 Equipment

- Plastic containers
- Analytical balance with an accuracy of ± 0.1 mg
- Plastic columns (BioRad)
- Teflon beakers
- Teflon-coated magnetic rotor assembling silver disk holder
- Hot plate with magnetic stirrer
- Alpha spectrometry
- Atomic absorption spectroscopy (AAS)

2.2 Tracers

- ^{209}Po (4.54 dpm g^{-1})
- Stable Pb (extra low ^{210}Pb background) (5 mg mL^{-1})

2.3 Chemical reagents

- Hydrochloric acid (HCl)
- Ammonium hydroxide (NH_4OH)
- Nitric acid (HNO_3)
- Perchloric acid ($HClO_4$)
- Ascorbic acid ($C_6H_8O_6$, powder form)
- Hydroxylamine hydrochloride
- Sodium citrate
- Anion exchange resin (AG 1-X8)

2.4 Solutions

- 25 mg Fe mL^{-1}, using $FeCl_3 \cdot 6H_2O$ to prepare
- 25 mg Pb mL^{-1}, using $Pb(NO3)_2$ with extra low ^{210}Pb to prepare

3 PROCEDURE

3.1 Separation of dissolved and particulate Po and Pb

1. 8-20 L seawater filtering through the polycarbonate membrane with 0.4 or 0.8 μm pore size, particulate matter, after washing with Milli-Q water, retained on the membrane is operationally defined as particulate sample for measuring Po and Pb, the filtration is defined as the dissolved sample for measuring Po and Pb.
2. Add the dissolved sample with concentrated HCl until the pH value is less than 2.0.
3. Particulate sample is kept at 18°C.

3.2 Pre-concentration of dissolved Po and Pb

1. Add pre-weighed ^{209}Po spike, usually ~1 dpm for 10 L water.
2. Add stable Pb carrier (i.e. $Pb(NO3)_2$ with very low ^{210}Pb background), usually 3 mg Pb for 20 L water.
3. Homogenize the sample and equilibrate for 24 hours with regular mixing.
4. Add Fe^{3+} carrier (i.e. $FeCl_3$ with extra low ^{210}Pb background), usually 5 mg Fe L^{-1}.
5. Add ammonium hydroxide to a pH of 8.5-9.0 to form $Fe(OH)_3$, and the sample is left for no less than 10 hours.
6. Siphon off the supernatant, separate the precipitate from the solution by centrifugation.

3.3 Digestion of particulate Po and Pb

1. Particulate sample is added stable Pb carrier (3 mg Pb for each sample) and ^{209}Po spike (~0.5 dpm for 10 L water).
2. Digest particulate sample with mixed HF, HNO_3, $HClO_4$ to a clean solution, and evaporating to nearly dryness.
3. Add 5 ml concentrated HCl and evaporating to nearly dryness.

3.4 Auto-plating of Po on silver disk

1. Dissolved the pre-concentrated dissolved and digested particulate samples with 6 M HCl, and adjusted to a pH range of 0-2.0 with ammonium hydroxide.
2. Add ascorbic acid to a colorless solution, then adding 1 ml 20% hydroxylamine hydrochloride and adjusted to a pH ~1.5.
3. Place the silver disk in a Teflon-coated magnetic rotor with one side free of touching the solution.

4. The Po isotopes (i.e. ^{209}Po and ^{210}Po) are auto-plated onto a silver disk at 95°C for 4 hours with stirring on a stirring plate.
5. The residual solution is dried completely and taken in 5 ml of 9 M HCl for separating of residual Po from Pb using an anion-exchange column (AG 1-X8). The purified Pb is spiked with ^{209}Po and stored for 1-2 years.

3.5 Deposition of in-growth Po

Auto-plate the in-growth ^{210}Po from ^{210}Pb decaying on silver disk with the same conditions to the first deposition. And the second deposition of Po is used to calculate ^{210}Pb activity in original seawater.

3.6 Measurement of Po

Count Po isotopes (i.e. ^{209}Po and ^{210}Po) using alpha-spectrometry, for ^{209}Po and ^{210}Po the energy are 4.881 MeV and 5.115 MeV respectively.

3.7 ^{210}Pb yield determination

An aliquot of the solution after the second Po deposition is taken to determining the recovered stable Pb using AAS. The volume of adopted depends on the detection limit of AAS.

3.8 ^{210}Po and ^{210}Pb activities calculation

^{210}Pb and ^{210}Po activities at sampling time can then be calculated applying in-growth, decay and recovery corrections following Rigaud et al., (2013).

4 REFERENCES

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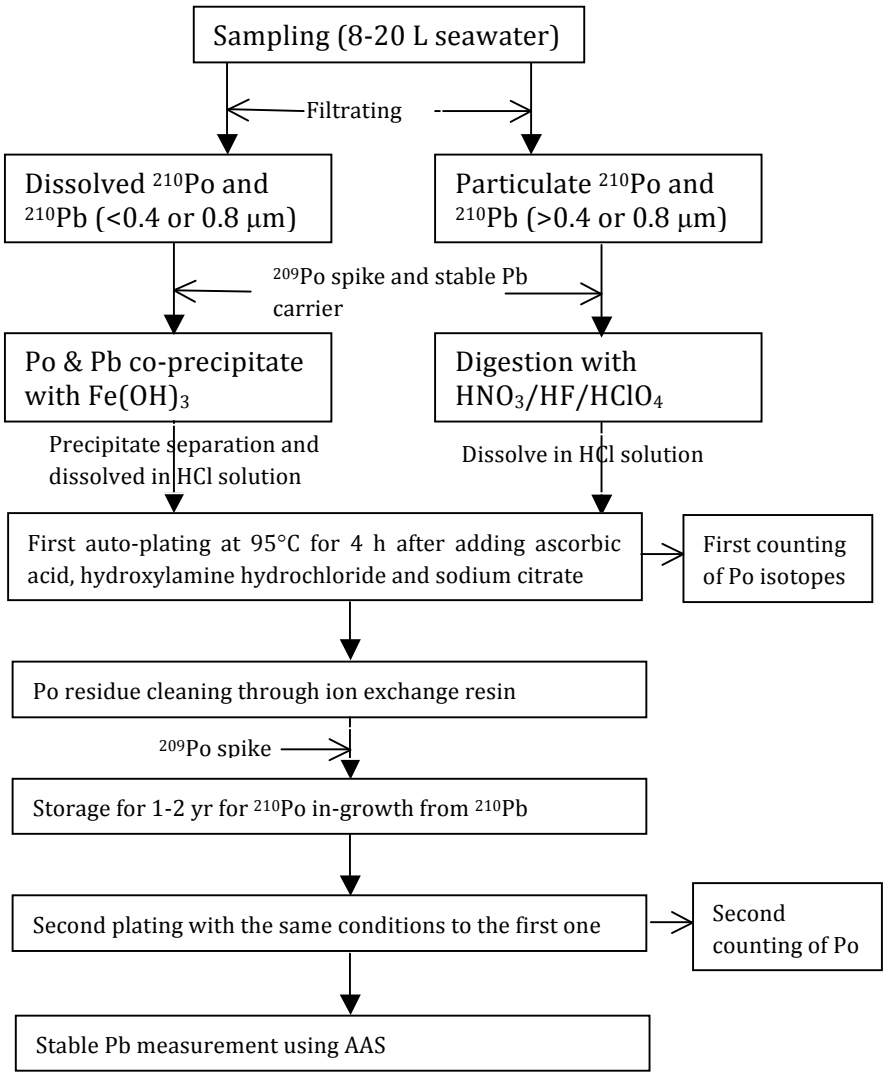
5 FLOW CHART


Sampling (8-20 L seawater)
Filtrating
Dissolved ^{210}Po and ^{210}Pb (<0.4 or 0.8 μm)
Particulate ^{210}Po and ^{210}Pb (>0.4 or 0.8 μm)
^{209}Po spike and stable Pb carrier
Po & Pb co-precipitate with $Fe(OH)_3$
Digestion with HNO_3/HF/$HClO_4$
Precipitate separation and dissolved in HCl solution
Dissolve in HCl solution
First auto-plating at 95°C for 4 h after adding ascorbic acid, hydroxylamine hydrochloride and sodium citrate
First counting of Po isotopes
Po residue cleaning through ion exchange resin
^{209}Po spike
Storage for 1-2 yr for ^{210}Po in-growth from ^{210}Pb
Second plating with the same conditions to the first one
Second counting of Po
Stable Pb measurement using AAS