1. Scope

This procedure describes a method for the concentration and measurement of Cs-134/7 in aqueous samples (surface, ground and sea water samples).

2. Summary

Cesium is concentrated and separated using AMP-PAN or KNiFC-PAN Resin prior to gamma spectrometry counting. AMP-PAN or KNiFC-PAN Resin are used to concentrate cesium from up to 100L aqueous samples. Flow rates up to 300 mL/min may be employed (Kameník et al., 2012; Pike et al., 2013).

AMP-PAN may be used for neutral and acidic samples (up to 1M HNO_3), KNIFC-PAN for neutral and slightly alkaline samples (Brewer et al., 1999; Kameník et al., 2012; Kameník & Ŝebesta, 2003).

Stable cesium can be used to monitor method yields and correct results to improve precision and accuracy (Kameník et al., 2012; Pike et al., 2013). Ideally the Cs content should be determined by ICP-MS, however atomic absorption or emission techniques may also be used, the amount of Cs carrier added will need to be adjusted accordingly.

For 100L samples and 50-70h counting the following MDAs were reported (Kameník et al., 2012): 0.18 $Bq.m^{-3}$ for Cs-134, 0.15 $Bq.m^{-3}$ for Cs-137.

3. Significance of use

This method is a rapid and reliable method for measurement of Cs-134/7 in aqueous samples.

4. Interferences

Large amounts of Na and K will not interfere with Cs uptake as long as the Cs content of the sample is small compared to the Cs capacity of the resin (64 mg Cs/g wet resin for AMP-PAN (Pike et al., 2013) and 256 mg Cs/g dry KNiFC-PAN resin (Kameník & Ŝebesta, 2003) – or 69 mg Cs/mL wet KNiFC-PAN resin (Kameník & Ŝebesta, 2003)).

5. Apparatus

1. Column or cartridge with appropriate holder or rack
2. Suitable reservoir or pump system
3. Gamma pulse height analyzer
4. Petri dishes

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5. Beakers
6. IR lamp

6. Reagents

a. Reagents

1. Deionized water.
2. Ethanol (EtOH)
3. Nitric acid (15.7 M)- concentrated HNO3 (sp gr 1.42)
4. Optional: CsCl
5. Optional: NaOH
6. Optional: NH_4OH
7. AMP-PAN or KNiFC-PAN Resin: M grade, bulk resin or pre-packed columns

b. Preparation of solutions

- 0.1 M HNO_3: For 100 mL solution add around 50 mL deionized water at the bottom of the 100 mL flask and add slowly 0.64 mL concentrated HNO_3 (69% HNO_3). Then, add water to the volumetric flask until the total volume. Mix thoroughly.
- Cs carrier (1 mg/mL): Dissolve 126,7 mg of CsCl in 50 mL water and dilute to 100mL with water
- 5 M NaOH: Dissolve 199.95 g NaOH pellets in 600 mL of water and dilute to 1 liter with water
- 5 M NH_4OH: Dissolve 175 g NH4OH in 600 mL of water and dilute to 1 liter with water

7. Procedure

a. Sample preparation

1. Measure the sample volume using a suitable mean, sample volumes up to 100 L may be analyzed (Kameník et al., 2012).
2. If necessary filter the sample
3. Acidify the sample using concentrated nitric acid (6 mL conc. HNO_3 per L of sample).

⚠ **Note**: Alternatively the sample can be loaded without acidification when using KNiFC-PAN

4. Optional: Add 1 ml of 1 mg/ml cesium carrier (for yield determination via ICP-MS) into each sample aliquot. The amount of Cs added may need to be adjusted in function of sample volume and sensitivity of the ICP-MS
5. Homogenize sample

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6. Optional: Withdraw suitable aliquot for ICP-MS determination of initial Cs content, the size of the aliquot will depend on Cs content and sample volume. For 100 L samples and 1 mg Cs typically a volume of 5 mL is withdrawn
7. Place columns or cartridges on rack or into suitable pumping system. Attach suitable reservoirs or tubing
8. Ensure that a container is below each column/cartridge

b. Radiochemical separation

1. Add at least 10 ml of 0.1 M HNO_3 to each column/cartridge to condition columns, allow to soak
2. Slurry an appropriate amount of AMP-PAN or KNiFC-PAN in 0.1M HNO_3. The exact amount of resin will depend on the sample size, typically a resin bed of 5 mL is used for 20 L samples, 25 mL for 100 L samples (rule of thumb: 1 mL resin per 4 L of sample)

⚠ **Note:** The resins have the following densities: AMP-PAN: 0.27 g dry resin/mL; ~1g wet resin/mL; KNiFC- PAN: 0.20 g dry resin/mL; ~1g wet resin/mL

3. Transfer slurry into column and allow to settle. Adjust amount of resin added to the columns to obtain desired bed volume.
4. Allow supernatant to drain.
5. Adjust flow rate to ≤ 300 mL/min (the optimum flow rate is in the order of 35 – 40 mL/min).
6. Place fresh sample container below the columns/cartridges
7. Load each sample onto the appropriate columns/cartridges and allow to drain.
8. Optional: Homogenize collected sample feed solution and withdraw suitably sized aliquot for yield determination (see step 6 section a)
9. Rinse columns/cartridges with two times 10 ml of 0.1 M HNO_3 (AMP-PAN) or deionized water (KNiFC-PAN). Allow to drain
10. Remove tubing/reservoir
11. Transfer resin into suitable beaker using EtOH rinses

⚠ **Note:** Alternatively Cs might be eluted from the column using 5 M NH_4Cl or 5 M NaOH. For AMP-PAN e.g. 10 bed volumes elute ~90% of the sorbed Cesium, 10 bed volumes of 5 M NaOH will remove a slightly higher amount (Šebesta & Štefula, 1990)

12. Carefully agitate resin/EtOH (e.g. using an orbital shaker) to homogenize the resin

c. Sample measurement

1. Dry resin under IR lamp

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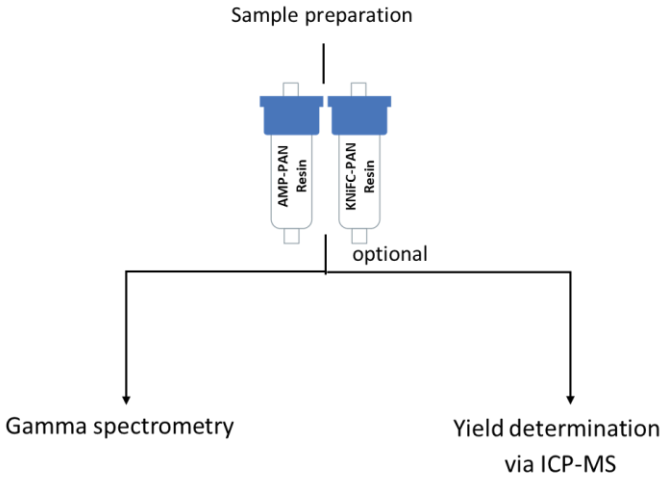
2. Transfer dried resin into suitable Petri dish assuring a homogeneous thickness of the resin layer.
3. Count sample on gamma spectrometer, adjust counting time in function of detection limit to be obtained.

⚠ **Note:** Calibration sources are prepared using identical amounts of resin homogeneously spiked with a traceable Cs-137 standard solution.

d. Synopsis



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