

1. Scope

With respect to their volatility, quantifying Cl-36 and I-129 is vital for the monitoring long-lived radionuclides, especially in nuclear facilities. Their accurate determination in radioactive waste is crucial for effective nuclear waste management and the safe storage of this waste in designated facilities. This procedure describes the separation of chloride and iodide from a range of different matrices.

2. Summary

After suitable sample preparation Cl-36 and I-129 are, if needed, reduced to chloride and iodide, and then loaded onto Ag⁺ loaded CL Resin which retains both. The analytes can then be purified and eluted separately in small volumes of suitable eluting agents. The selective extraction of Cl-36 and I-129 aims to reduce the time required for their chemical separation of these chemically very similar elements. Further, using extraction chromatography allows strongly decreasing volumes of reagents required for the separation process, thus reducing waste that might contain radioactive materials. The method simplifies sample preparation compared to traditional techniques, improving accuracy and efficiency. Studies reported by (Warwick et al., 2010; Zulauf, Happel, Mokili, Bombard, et al., 2010; Zulauf, Happel, Mokili, Warwick, et al., 2010; Zulauf & Happel, 2010) provide detailed CL Resin characterization, including distribution coefficients for chloride and iodide, and demonstrate its potential for nuclear waste monitoring and management.

3. Significance of use

This method describes a rapid and facile radiochemical separation of Cl-36 and I-129 which might be present in decommissioning samples using CL Resin.

4. Interferences

Interferences identified in various studies stem from two main effects: chemical influences on the separation and the presence of other radionuclides in real samples that may affect the quantification of Cl-36 and/or I-129. Potential interfering elements during chemical separation include Ag (as the resin is loaded with this element), Pd and strong oxidizing agents. High concentrations of OH⁻ will interfere with the retention of Cl-36. Additionally, radionuclides that could interfere with Cl-36 and I-129 quantification, particularly via LSC, include ³H, ¹⁴C and ³⁵S.

5. Apparatus

- Analytical balance- 0.0001 g sensitivity
 - Beaker (10 mL, 50 mL)
 - Vortex mixer
 - 20 mL PE vials
 - Pipettes
 - Fume hood
 - Hotplate
 - Column reservoirs - 25 mL, Part number AC-120
 - Column rack - Part number AC-104
- Alternatively:
- Vacuum box or vacuum bottle with column adaptor
 - Vacuum pump

6. Reagents

a. Reagents

All references to water should be understood to mean deionized water.

- Bulk CL resin or CL resin columns –CL resin supplied **NOT** loaded with Ag⁺
 - 1 M sulfuric acid (alternatively HNO₃ may be used)
 - Optional: 0.1 M SnSO₄ solution
 - Ag load solution (20 mg.mL⁻¹) - Dissolve 787,4 mg AgNO₃ in 25 mL water
 - 0.1M NH₄SCN solution (alternatively 0.1M NaSCN might be used)
 - 1% (w/w) NaOH solution
 - 0.35 M Na₂S solution
- ⚠ **Note 1:** all work with the Na₂S should be performed in a fume hood, including the addition of the liquid scintillation cocktail.
- Liquid scintillation cocktail
- ⚠ **Note 2:** Some LSC cocktails may reduce traces of Ag⁺ co-eluted from the column resulting in 'blackened' LSC samples, it is thus advisable to test your cocktail before use. ProSafe HC was found to be suited.

b. Preparation of solutions

- 1 M H₂SO₄: For 100 mL solution add around 50 mL deionized water at the bottom of the 100 mL flask and add slowly 5.60 mL concentrated H₂SO₄ (96% H₂SO₄). Then, add water to the volumetric flask until the total volume. Mix thoroughly.

- **6 mM Na₂CO₃:** For 100 mL solution add around 40 mL deionized water at the bottom of the 100 mL flask and add slowly 0.0636 g of Na₂CO₃ (anhydrous). Then, add water to the volumetric flask until the total volume. Mix thoroughly.
 - **1 M NaOH:** For 100 mL solution add around 40 mL deionized water at the bottom of the 100 mL flask and add slowly 4 g of NaOH (special attention to hygroscopicity of the substance, NaOH can absorb humidity in the air). Then, add water to the volumetric flask until the total volume. Mix thoroughly.
 - **0.1 M SnSO₄:** For 100 mL solution add around 40 mL deionized water at the bottom of the 100 mL flask and add slowly 2.15 g of SnSO₄ (anhydrous). Then, add water to the volumetric flask until the total volume. Mix thoroughly.
- ⚠ **Note:** SnSO₄ may be partially insoluble in water depending on the pH. If this occurs, adjust the pH or dissolve it in a diluted acid (such as 0.1 M H₂SO₄).

7. Procedure

a. Sample preparation

Column preparation (alternatively use pre-packed CL columns):

1. Weigh 0.65 g of the resin into a 20 mL PE vial
 2. Add 5 mL of 1 M sulfuric acid and soak for at least 30 min, preferably while shaking
 3. Pack 2 mL standard column with the soaked resin
 4. Add 1 mL of Ag⁺ load solution onto the column. Allow the solution to load onto the column, then close the lower end of the column to stop the flow. Let the column stand for more than 30 min in order to allow for Ag uptake.
- ⚠ **Note 3:** Alternatively, the Cl resin might also be loaded with Ag⁺ in batch mode; in this case perform steps 1 and 2, then add 1 mL Ag⁺ load solution into the PE vial, cap and shake for another 30 min (preferably longer). Transfer the Ag⁺ loaded resin into a 2 mL standard column
5. Add 5 mL 1 M H₂SO₄ onto the column and open the lower end of the column. Allow the solution to pass
- ⚠ **Note 4:** In case the sample is loaded in 6 mM Na₂CO₃ soak resin in water and rinse column with water instead of 1 M H₂SO₄; rinse until the eluate is free of acid.

Sample preparation:

- Water samples: evaporate sample to a volume of approx. 10 mL, adjust to 1 M sulfuric acid
- ⚠ **Note 5:** 1 M sulfuric acid is chosen as Ag⁺ retention is optimal under these conditions, near neutral pH is also acceptable
- Bubbler solutions:
 - 0.1 M and 1 M NaOH solutions should be at least neutralized using sulfuric acid, preferably the loading solutions should be adjusted to 1 M H₂SO₄

- ⚠ **Note 6:** in case only I-129 is to be analysed the NaOH solutions can be used as they are without adjustment
 - 6 mM Na₂CO₃ solutions can be employed as they are, no adjustment is necessary
 - Solid residues: Dissolve residue in 5 mL 1 M sulfuric acid
- ⚠ **Note 7:** The concentration of natural Cl⁻ and I⁻ should preferably be determined in the sample load solution e.g. by ion chromatography
- ⚠ **Note 8:** In order to assure that Cl and I are present in the sample as chloride and iodide it is advisable to additionally add a reducing agent (e.g. 0.1 M SnSO₄) to the sample loading solution

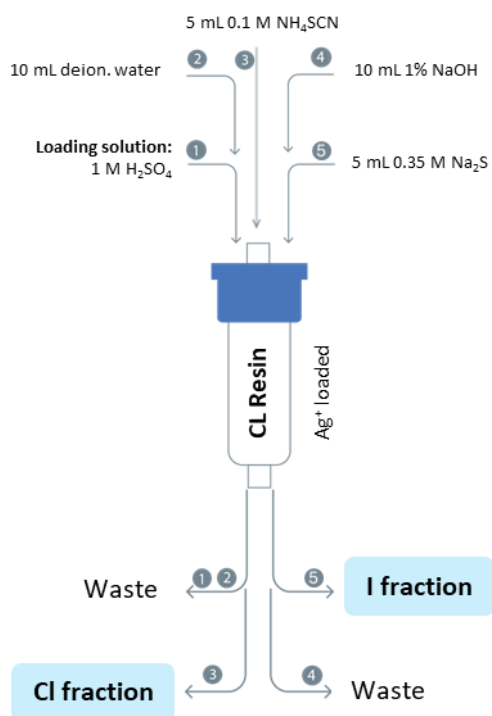
b. Radiochemical separation

1. Load sample onto column and allow to drain.
2. Rinse beaker with 5 mL 1 M sulfuric acid (optional: deionized water) and add onto the column.
- ⚠ **Note 9:** In case the sample was loaded in 6 mM Na₂CO₃ deionized water must be used instead of 1 M H₂SO₄
3. Rinse column with 2 x 5 mL deionised water. Discard eluates.
- ⚠ **Note 10:** In case the sample was loaded in 6 mM Na₂CO₃ the column should be rinsed with 5 mL 0.1 M H₂SO₄ between both water rinsing steps in order to improve C-14 removal
4. Place fresh 20 mL PE vial below column.
5. Elute Cl⁻ with 5 mL 0.1 M NH₄SCN.
6. Optional: take aliquot for Cl content determination in order to allow for yield determination
7. Replace LSC vial by waste container
8. Rinse column with 10 mL 1% NaOH
9. Place fresh 20 mL PE vial below column
10. Elute I⁻ with 5 mL 0.35 M Na₂S
11. Optional: take aliquot for I content determination in order to allow for yield determination

c. Sample measurement

1. Add 10 mL LSC cocktail to the vials containing the eluted solution for Cl and I fractions and shake vigorously

d. Synopsis of the separation



8. References

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