Sample Preparation Method for Low-Level Total ^{129}I Measurements by ICP-MS

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Summary

Trace-level measurements of iodine's isotopic (^{129}I and ^{127}I) and chemical species distributions are needed for an accurate understanding of radioiodine migration in the Hanford subsurface. Pacific Northwest National Laboratory (PNNL) previously developed a novel analytical method for iodine characterization that uses ion chromatography (IC) coupled to inductively coupled mass spectrometry (ICP-MS). While the method can measure speciated forms of ^{129}I at levels below the drinking water standard, an interference from molybdenum (Mo) prevents the assay from quantifying the <u>total</u> ^{129}I concentration in many Hanford sample matrices. In this work, solvent extraction was evaluated as a sample preparation method for eliminating the Mo interference. A series of 10 experiments was conducted in which solutions containing known amounts of iodate or iodide were treated by solvent extraction, and the extracted solutions were analyzed for total iodine concentrations by ICP-MS. Several extraction parameters such as reagent concentrations and chemical reaction times were systematically adjusted in attempts to optimize the extraction process. While solvent extraction was shown to be effective at removing Mo, there was a consistent inability to recover more than approximately 75% of the total iodine in most experiments. This would reduce the ability to detect ^{129}I at levels near the drinking water standard. Additionally, the extraction efficiencies in several experiments were highly variable, suggesting that solvent extraction could add significant uncertainty to radioiodine measurements. We recommend evaluating ion exchange as an alternative sample preparation approach in fiscal year (FY) 2024.

Introduction

Iodine isotopes, including long half-life ^{129}I (15.7 million years), were formed as a byproduct of nuclear fission at the Hanford Site's nine reactors. Liquid wastes from plutonium production were discharged to the soil (e.g., from disposal sites and leaking underground storage tanks), resulting in contaminated sediments and dilute ^{129}I groundwater plumes encompassing an area over 50 km^2 in the Hanford Central Plateau. Iodine is believed to be present as iodide, iodate, and organo-iodine species (Qafoku et al. 2018), and their distribution affects plume behavior due to the species' different sorption characteristics. Therefore, quantifying the chemical forms of iodine is important for predicting radioiodine migration in the subsurface.

In FY19-20, PNNL developed a novel, rapid technique for simultaneous iodine speciation (iodide/iodate) and isotopic ratio (^{129}I/^{127}I) measurements using IC coupled to ICP-MS (Kimmig et al. 2021). While the method can accurately measure ^{129}I-iodate and ^{129}I-iodide at levels below the drinking water standard (1 pCi/L or ~5.6 ng/L), interference from Mo prevents the method from determining total ^{129}I in many Hanford groundwater and sediment matrices.

The objective of this work is to develop a sample preparation method that eliminates the Mo interference from measurements of total ^{129}I by ICP-MS. This will increase the versatility of the analytical method and could provide additional insights about radioiodine speciation at Hanford (e.g., evaluate the presence of organo-iodine). Two candidate sample preparation approaches were considered: solvent extraction and

preparative ion-exchange chromatography. Solvent extraction was chosen for evaluation in FY23 based on a previous PNNL study that used solvent extraction to separate iodine species from Hanford tank waste (Soderquist et al. 2021).
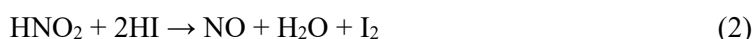
Iodine Separation by Solvent Extraction

The basis for iodine separation by solvent extraction is the high solubility of molecular iodine (I_2) in nonpolar organic solvents such as carbon tetrachloride (CCl_4). Iodide and iodate in an aqueous sample can be converted to I_2 by oxidation and reduction reactions, and the I_2 can then be extracted into CCl_4. Most ionic sample components, such as dissolved metals and anions, are insoluble in CCl_4 and should be left behind in the aqueous phase. Extracted iodine is then back-extracted from the CCl_4 by converting the I_2 to iodide using an aqueous reducing agent.

The strategy for converting iodate to I_2 has two steps. First, the sample is reacted with sodium sulfite (Na_2SO_3) to produce iodide:

$$IO_3^- + 3SO_3^{2-} \rightarrow I^- + 3SO_4^{2-} \tag{1}$$

Next, the iodide is oxidized to I_2 using sodium nitrite ($NaNO_2$):

$$HNO_2 + 2HI \rightarrow NO + H_2O + I_2 \tag{2}$$

The $NaNO_2$ reaction (2) is also used for samples that contain iodide at the outset. Back-extraction of I_2 from CCl_4 into H_2O is facilitated by reaction with Na_2SO_3:

$$I_2 + SO_3^{2-} + H_2O \rightarrow 2I^- + SO_4^{2-} + 2H^+ \tag{3}$$
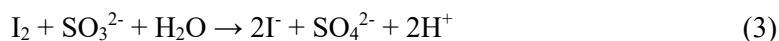
Solvent extractions in this work were performed in glass separation funnels. The general procedure consisted of 15 steps:

1. Add a measured amount (~45 mL) of sample and 5 mL of CCl_4 to a 60-mL separation funnel (Funnel A).
2. Add concentrated nitric acid to Funnel A to acidify the solution.
3. Add the appropriate redox reagents ($NaNO_2$ or Na_2SO_3 followed by $NaNO_2$) to Funnel A.
4. Vigorously mix the contents of Funnel A and allow the solution to react for a designated time interval (nominally 5 min.).
5. Dispense the lower (CCl_4) phase from Funnel A into a clean 30-mL separation funnel (Funnel B).
6. Add 5 mL of CCl_4 to Funnel A.
7. Vigorously mix the contents of Funnel A and allow the solution to settle for the designated time interval.
8. Dispense the CCl_4 phase from Funnel A into Funnel B.
9. Add 1 mL of deionized (DI) water and 0.020 mL of a designated concentration of Na_2SO_3 solution to Funnel B.
10. Vigorously mix the contents of Funnel B and allow the solution to settle for 2 min.
11. Dispense the CCl_4 from Funnel B into a clean 30-mL separation funnel (Funnel C).
12. Add 1 mL of DI water to Funnel C.
13. Vigorously mix the contents of Funnel C and allow the solution to settle for 1 min.
14. Dispense the CCl_4 phase from Funnel C to a waste container.
15. Combine the aqueous phases from Funnel A and Funnel B – this is the back-extracted sample, which has an approximate volume of 2.02 mL.

Modifications to this procedure for troubleshooting purposes are noted below. All iodide and iodate samples were prepared using ^{127}I (nonradioactive) standards to eliminate the need for handling radioactive materials and to reduce waste disposal costs.

Solvent extraction performance was evaluated by extracting samples containing known amounts of iodate and/or iodide and measuring the concentrations of iodine in the back-extracted solutions by ICP-MS. In some cases, Mo was included in the samples to verify that iodine can effectively be separated from Mo by solvent extraction. For each-extracted sample, the percent recovery was calculated from the quantity of iodine that was back-extracted relative to the initial amount in the sample.

FY23 Progress

A series of 10 experiments was conducted to evaluate the viability of solvent extraction as a sample preparation method for trace-level, total iodine measurements by ICP-MS. The first experiment focused on introducing analysts to solvent extraction operations and was not quantitative; those results are not included in this report. The remaining experiments are summarized in Table 1 and are discussed below.

Table 1. Iodine Solvent Extraction Experiments[a]

Expt.	Objective(s)	Results
2	Initial quantitative evaluation	Iodate recovery: 0%, 0% Iodide recovery: 0.2%, 0.5%
3	Initial quantitative evaluation at low pH conditions	Iodate recovery: 0.3%, 0.2% Iodide recovery: 103%, 97%
4	Troubleshoot iodate extraction with visual detection	Successful extraction confirmed by color changes
5	a. Evaluate iodate extraction recovery under baseline conditions b. Demonstrate separation of iodine from a sample containing 10 µg/L Mo c. Evaluate effect of doubling redox reagent concentrations (1 M vs. 2 M) on recoveries from 5 µg/L iodate solutions	a. Iodate recovery: 64% b. Mo concentrations in extracted sample: (0.07 µg/L) c. 1 M redox recovery: 64% 2 M redox recovery: 59%
6	Evaluate effect of reaction time (5, 10, 20 min.) on recoveries from 5-µg/L iodate solutions	5 min. recovery: 54% 10 min. recovery: 61% 20 min. recovery: 52%

7	a. Evaluate effect of doubling redox reagent concentrations and/or nitric acid concentration on recoveries from 5-µg/L iodate solutions
	
	b. Determine the speciation of iodine in unextracted aqueous fractions (5-µg/L iodate starting solutions)
		a. Baseline recovery: 61%
		   1 M redox, 2x nitric acid recovery: 75%
		   2 M redox, 1x nitic acid recovery: 76%
		   2 M redox, 2x nitric acid recovery: 82%
		
		b. Iodate 9-25% of total unextracted iodine
		   Iodide 75-91% of total unextracted iodine

8	a. Determine the amount of iodine extracted in each of three CCl_4 extraction steps from 5-µg/L iodate solutions
	
	b. Evaluate effect of increasing $NaNO_2$ by 1.5x and 2x
	
	c. Evaluate effect of a second addition of $NaNO_2$ and two additional CCl_4 extractions
		a. Recovery after 1st extraction: 45%
		   Recovery after 2nd extraction: 69%
		   Recovery after 3rd extraction: 70%
		b. Baseline recovery: 69%
		   1.5x $NaNO_2$ recovery: 63%
		   2.0x $NaNO_2$ recovery: 57%
		c. 1 addition $NaNO_2$ recovery: 64%
		   2 addition $NaNO_2$ recovery: 73%

9	Evaluate reproducibility of expt. 3 iodide recoveries	Expt. 3 iodide recovery: 103%, 97% Expt. 9 iodide recovery: 67%, 64%
10	Evaluate whether personnel-specific operations were affecting iodide recoveries	Analyst 1 recovery: 65%, 94% Analyst 2 recovery: 74%, 82%

(a) Percent recovery values are shown for each sample that was processed (two values are shown in cases where replicate samples were extracted).

Initial Quantitative Evaluation

Initial tests (experiments 2 and 3) involved extracting separate aqueous solutions containing 5 µg/L of iodate or 5 µg/L of iodide. A preparation blank (DI water sample) was also extracted to check for possible contamination from reagents and glassware. Essentially no iodine (0.0-0.5%) was recovered in the experiment 2 extractions, which was determined to be caused by neutral pH conditions (step 2 of the procedure had not been implemented yet). The reaction between iodide and nitrite (reaction 2) requires an acidic medium to proceed rapidly (Abeledo et al. 1931). In experiment 3, the extractions were repeated with concentrated nitric acid added to adjust the pH to approximately 1.4. The resulting iodide solution recoveries were 97% and 103%, while the iodate solution recoveries were 0%. An incorrect reagent addition (e.g., adding $NaNO_2$ to the sample instead of Na_2SO_3) was suspected to be the cause of the failed iodate extractions.

Iodate Troubleshooting

The next six experiments focused on troubleshooting the extraction of iodine from iodate solutions. In experiment 4, a highly concentrated (100 mg/L) iodate solution was processed to provide visual confirmation that the redox reactions and extraction steps were proceeding as expected. At sufficiently high concentrations, molecular iodine has a deep violet color when dissolved in organic solvents such as CCl_4. Figure 1 shows photographs taken during experiment 4 at different stages of the extraction procedure. In panel A, the sample had been reacted with sodium sulfite and then sodium nitrite to convert iodate to I_2. The pink color in the lower portion of the separation funnel (CCl_4 phase) indicates that some I_2 has been extracted into CCl_4, while the brown color in the upper portion of the separation funnel (aqueous phase) likely indicates a mixture of iodide, I_2, and triiodide (I_3^-). Triiodide forms in aqueous solutions containing iodide and I_2 and has a brown color. Panel B shows the solution after the second CCl_4 extraction (step 7). The lighter color of the aqueous phase provides evidence that most of the I_2 had extracted into CCl_4. Finally, panel C shows the solution after the first back-extraction (step 10). The clear color of the CCl_4 phase demonstrates that I_2 had effectively been back-extracted into the aqueous phase as iodide. While this experiment was qualitative only (no ICP-MS analyses were performed on the extracted solutions), the color changes demonstrated that iodine can successfully be extracted from iodate solutions using our protocol.
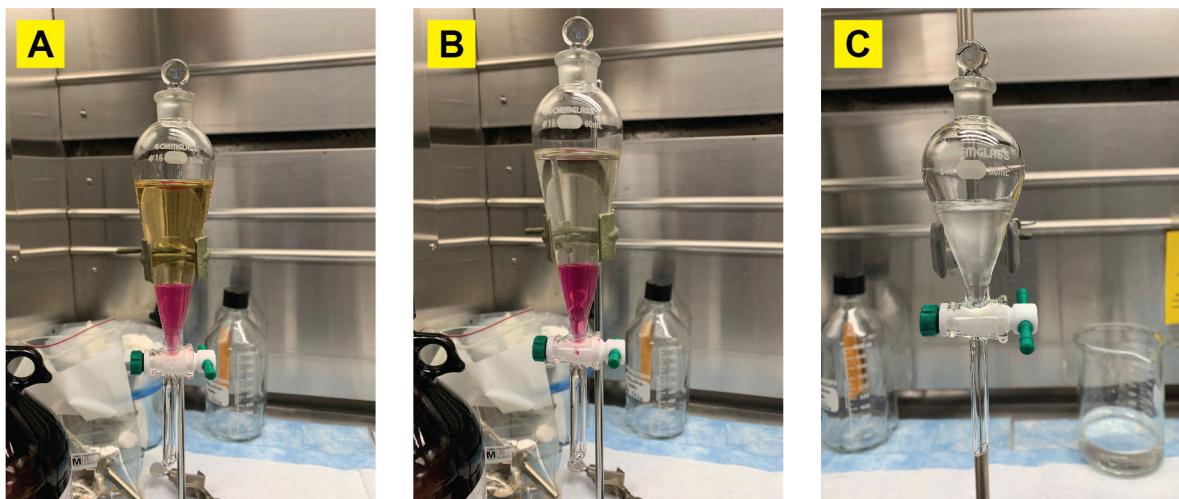

Figure 1. Photographs taken during experiment 4, solvent extraction of a 100-mg/L iodate solution: A) after step 4, B) after step 7, and C) after step 10.

Experiments 5-9 were focused on quantifying and optimizing the recoveries from iodate solutions. Concentrations of iodate in all tests were approximately 5 µg/L, which is a convenient level for analysis by ICP-MS. In experiment 5, a set of "baseline" conditions was established – this included the use of 1 M solutions of sodium nitrite and sodium sulfite, 5-minute reaction periods, and acidification with 0.100 mL of concentrated nitric acid (corresponding to a pH of approximately 1.4). Under these baseline conditions, the iodine recovery was 64%. A solution containing approximately 5 µg/L of iodate and 10 µg/L Mo was also extracted in experiment 5 to determine whether iodine is effectively separated from Mo by solvent extraction. The level of Mo in the back-extracted solution was very low (0.07 µg/L), verifying that solvent extraction can effectively separate iodine from Mo (eliminating the Mo interference).

Several extraction parameters were adjusted in experiments 5-9 in attempts to increase the iodine recoveries. These included the concentrations of $NaNO_2$ and Na_2SO_3 (1 M vs. 2 M), amount of concentrated nitric acid (0.100 mL vs. 0.200 mL), reaction times (5, 10, 20 min.), and the number of CCl_4 extractions (2 vs. 3). Here are the highlights from these tests.

- The effect of increasing the reagent concentrations on extraction efficiency is unclear due to the variability across multiple experiments. In one test (experiment 5), doubling the amounts of all redox reagents did not improve the recoveries. However, in a subsequent test (experiment 7), doubling the amount of nitric acid and/or the amounts of $NaNO_2$ and Na_2SO_3 increased the recoveries from 61% (baseline conditions) to 75-82%. Later tests using the doubled acid concentration (experiments 8 and 9) with other parameters remaining the same had intermediate recoveries ranging from 64-69%.

- For the three reaction times tested (5, 10, and 20 min.), the highest recovery (61%) was obtained with a 10-min. reaction period. However, the 10-min. recovery was slightly lower than those obtained in previous experiments using 5-min. reaction times. Therefore, 5-min. reaction times continued to be used in subsequent experiments.

- Increasing the number of CCl_4 extractions from two to three did not significantly improve the recovery (69% for two extraction steps and 70% for three extraction steps).

To help understand why the iodate extractions were incomplete, an iodine speciation analysis (IC-ICP-MS) was performed on the aqueous phase after the second CCl_4 extraction (step 7) for the samples in one of the experiments in which baseline conditions were compared against those with doubled reagent concentrations (experiment 7). Iodide was the predominant species, accounting for 75-91% of the unextracted iodine. This suggested that the conversion of iodate to iodide (reaction 1) was mostly complete, and the limiting factor was incomplete conversion of iodide to I_2 (reaction 2). Consequently, in experiment 8, two attempts were made to enhance the production of I_2. The first attempt involved increasing the amounts of $NaNO_2$ added by factors of 1.5 and 2.0. This did not increase the recoveries over that obtained under baseline conditions. The second attempt involved making a second addition of $NaNO_2$ to Funnel A after step 8 of the procedure and extracting the aqueous phase two more times with separate 5-mL aliquots of CCl_4. This boosted the overall recovery from ~64% to 73% at the expense of additional sample manipulations and processing time.

Further Evaluation of Iodide Extraction Efficiency

The recoveries of iodine from iodide solutions for experiment 3 (noted above) were relatively high (97% and 103%) but were based on a small data set of two samples. To evaluate the reproducibility of these results, the iodide extractions were repeated by a different analyst under the same conditions in experiment 9. This second group of results had lower recoveries of 64% and 67%. Consequently, a third set of iodide extractions was performed with both analysts processing identical samples and observing each other for differences in technique (experiment 10). The first analyst obtained recoveries of 65% and 94%, while the second analyst recovered 74% and 82% of the total iodine. The 65% recovery result from

the first analyst appears to be an outlier that was attributed to accidentally dispensing excess fluid from the extraction vessel in step 11 of the procedure. Some minor differences in technique were noted by the two analysts in experiment 10 (e.g., variations in the way the separation funnels were shaken and differences in the way the final extracts were retrieved from the separation funnels), but those changes were not suspected to account for the spread in results.

Conclusion

Solvent extraction was shown to effectively separate iodine from Mo in aqueous samples. However, the body of results for this task demonstrates a consistent inability to fully extract all iodine, which would reduce the ability to detect ^{129}I at levels near the drinking water standard. Moreover, the large variability in recoveries in our experiments suggests that solvent extraction could add significant uncertainty to iodine measurements. Consequently, for FY24, we recommend evaluating ion exchange as an alternative sample preparation approach.

Planned FY24 Activities

Activities in FY24 will focus on developing a sample preparation method using ion exchange to remove the Mo interference. Sample solutions will be passed through a column containing an anion exchange resin such as AG1-X8, which will separate iodate and iodide from molybdate based on their different affinities for the resin. Effluent from the column will be analyzed for total radioiodine and Mo by ICP-MS, and the elution conditions (e.g., eluent pH) will be adjusted as needed to optimize the separation. This approach will be tested using chemical standards containing known amounts of ^{129}I-iodate, ^{129}I-iodide, and molybdate at concentrations relevant to Hanford sediments and groundwater. After the sample cleanup protocol has been developed, a limited number of Hanford groundwater and sediment samples containing ^{129}I will be processed and analyzed for total ^{129}I by ICP-MS. Results will be compared to speciation data determined by IC-ICP-MS.

Quality Assurance

This work was performed in accordance with the PNNL Nuclear Quality Assurance Program (NQAP). The NQAP complies with DOE Order 414.1D, *Quality Assurance*. The NQAP uses NQA-1-2012, *Quality Assurance Requirements for Nuclear Facility Application*, as its consensus standard and NQA-1-2012, Subpart 4.2.1, as the basis for its graded approach to quality. The data presented in this document is preliminary, For Information Only (FIO), and subject to revision.

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