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Measurement of Iodine, Iodide, and Iodate in Hanford Tank Waste

Technology Transfer from PNNL to Hanford 222-S Laboratory

September 2021

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Pacific Northwest National Laboratory
Richland, Washington 99354

Summary

This report describes the chemical separations used to measure the amount and chemical forms of inorganic iodine in Hanford tank waste and provides the technical basis and recommendations for transferring and implementing this new inorganic iodine analytical technique at Hanford's 222-S Laboratory. Part of the iodine in the tanks is fission product iodine-129, a long-lived beta emitter. Iodine is known to exist in the tanks in the forms of iodide and iodate, and perhaps periodate. The tanks may also have organic iodides, but their measurement is outside the scope of this report.

When the tank waste is converted into its final waste forms (such as glass or grout), it will undergo various unit operations such as filtration, cesium ion exchange, evaporation, and vitrification. Secondary waste streams are subjected to many other separation and conversion processes (adsorption, oxidation, reduction). The behavior of iodine in these processes depends on its chemical forms, which have not been previously measured. The various inorganic chemical forms of iodine are chemically reactive and will dissolve, precipitate, undergo redox reactions, evaporate, and condense in parts of the waste treatment process. Iodine-129 is radiotoxic, and its behavior must be known in the waste treatment process. Iodine-129 is regulated for air emissions and problematic for disposal.

Because tank waste is strongly basic, only a few inorganic chemical forms of iodine can be present, and the analyte list is short. At pH 12 to 14, iodine can exist as iodide, iodate, and periodate. All of the other oxidation states convert into one of these forms at the high pH of tank waste. Several iodides are insoluble in water and could conceivably exist as suspended solids in tank waste (AgI, PdI_2, CuI, Hg_2I_2), but this is unlikely because the concentrations of silver, palladium, copper, and mercury in the tank wastes are quite low, probably too low to materially affect the concentration of iodine in the tank waste supernatant liquid. Several iodates are sparingly soluble, but the concentration of iodate is quite low, almost certainty too low to form a precipitate. Inorganic iodine compounds may be mechanically occluded in tank waste solids. The water-insoluble sludge is believed to have only about 1% of the iodine in the tanks.[1] Traces of a silver-iodine compound have been found in the water-insoluble sludge from tank 241-C-105,[2] which the authors attributed to a silver reactor for offgas treatment that was flushed into this tank.

In a simple aqueous solution, iodate and iodide are straightforward to measure, but the raw tank waste has several oxidizing agents that could seriously interfere with the iodine redox chemistry, primarily nitrite and chromate. The iodide and iodate separation chemistry described in this report is designed to accommodate the tank waste composition.

To measure iodine, each chemical form of iodine is separated, in sequence, by a series of solvent extractions and redox reactions. Once isolated, the iodine is measured using inductively couple plasma mass spectrometry (ICP-MS). Both ^{127}I (stable iodine) and ^{129}I (long-lived beta emitter) are reported by the ICP-MS. Because stable iodine is an analyte, no iodine carrier can be used. The concentration of iodine in the raw tank waste is on the order of 1 ppm, which is high enough to comfortably separate and measure without using an iodine carrier.

Analysis of the chemical form of iodine in Hanford tank wastes was developed at Pacific Northwest National Laboratory and will be transferred to the Department of Energy's 222-S Laboratory on the Hanford Site, in Washington State, for implementation during waste processing operations.

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[1] Asmussen RM, TG Levitskaia, CL Bottenus, and MS Fountain. 2020. *Iodine Speciation Basis and Gap Analysis for Hanford Tank Farm Inventory and during Processing*. PNNL-30105 Rev. 0; RPT-OSIF-012 Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.

[2] Reynolds JG, JS Lachut, HK Meznarich, TM Ely, AM Templeton, GA Cooke, 2020. "Silver-Iodine Association in Hanford Nuclear Waste", *Journal of Radioanalytical and Nuclear Chemistry* 326, 737-741

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1.0 Introduction

This report formally transmits a new analytical method for measuring inorganic iodine in Hanford tank wastes to the Department of Energy 222-S Laboratory on the Hanford Site. This new method was developed at the Pacific Northwest National Laboratory (PNNL).

The Hanford waste tanks contain iodine, roughly 1 part per million. Total ^{129}I has been measured in many tanks and the data has been published. Stable iodine has not been measured in most tanks, and the chemical form of the iodine has not been measured until recently (Fountain 2020).

The amount and chemical form of iodine in tank waste needs to be known for the waste treatment processes and disposal pathways. When tank waste is processed for vitrification or grouting, the iodine will undergo chemical reactions. It will dissolve, precipitate, change oxidation states, evaporate, and condense. The chemical form of the iodine in the tank waste needs to be known so that the behavior of iodine can be accurately predicted during waste processing and anticipated in waste form disposal and offgas emissions. Iodine-129 is radioactive (15.7 million year half-life, 40 keV endpoint beta, 39.6 keV photon). Iodine concentrates in the thyroid and is radiotoxic, soluble in water, and mobile in the environment. The amount of stable iodine (^{127}I) in tank waste needs to be known so that the entire inventory of iodine can be accounted for in design and performance of abatement technologies (ion exchange, adsorption) to remove or immobilize ^{129}I.

The isotopes of interest in Hanford tank waste are ^{127}I (stable iodine) and ^{129}I (radioiodine). All of the other iodine isotopes are short-lived and have decayed to nothing. The chemical forms of interest are iodide, iodate, and periodate. All other inorganic forms of iodine under tank waste conditions will convert to iodide, iodate, and possibly periodate. In a neutral or acidic solution (such as a condensate), iodine may appear in the form of the free element (I_2) or tri-iodide.

Tank waste iodine is probably completely in solution, or in a soluble form trapped inside soluble saltcake. Several iodides are quite insoluble (AgI, PdI_2, CuI, Hg_2I_2), but tank waste has very little silver, palladium, copper, and mercury, too little to have much chance of precipitating iodide. Several iodates are also insoluble [$Zr(IO_3)_4$, $Th(IO_3)_4$, $Pu(IO_3)_4$], but the iodate concentration is low, and a tank supernate would not be expected to have enough zirconium, thorium, or plutonium to form an iodate precipitate. All of the work described in this report assumes tank waste supernate, not saltcake. The saltcake (which is soluble) may have mechanically occluded iodine compounds. The insoluble sludge is reported to have only about 1% of the total iodine inventory at Hanford (Asmussen et al. 2020).

Section 3.0 of this report describes the general inorganic and analytical chemistry of iodine. It describes previous ^{129}I analyses, the general outline of the new iodine analysis, and the redox chemistry of iodine used in the analytical separations.

Section 4.0 describes in detail the separation and measurement of the inorganic forms of iodine in tank waste. This section describes the exact mechanical and chemical operations necessary to perform the iodine analyses, using the chemistry previously described in Section 3.0.

Section 5.0 describes the calculations and data evaluation.

2.0 Quality Assurance

This work was conducted under Pacific Northwest National Laboratory (PNNL) project 77634, “River Protection Project Integrated Flowsheet Support,” with funding from Washington River Protection Solutions, LLC (WRPS) project 75268.

All research and development (R&D) work at PNNL is performed in accordance with PNNL’s Laboratory-level Quality Management Program, which provides overall guidance to staff based on a graded application of NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications*, to R&D activities. The quality assurance (QA) controls of the WRPS Waste Form Testing Program (WWFTP) QA program, which implements the requirements of NQA-1-2008, *Quality Assurance Requirements for Nuclear Facility Applications*, and NQA-1a-2009, *Addenda to ASME NQA-1-2008*, were also applied to this work. The WWFTP QA program includes procedures that provide detailed instructions for performing and documenting research activities and, consistent with the guidance provided by NQA-1, categorizes R&D work into three technology levels based on the amount of QA rigor required: Basic Research, Applied Research, and Development Work (in order of increasing rigor).

This report describes chemical separations techniques used to measure the amount and chemical forms of inorganic iodine in Hanford tank waste and provides the technical basis and recommendations for transferring and implementing these new analytical techniques at Hanford’s 222-S Laboratory. The preparation of this report was assigned the technology level “Basic Research” and was planned, performed, documented, reviewed, and reported in accordance with procedure QA-NSLW-1101, *Scientific Investigation for Basic Research*. The analytical work that supports this report is described in Fountain 2020, which documents the measurement of inorganic iodine species in raw waste samples from several Hanford waste tanks. Fountain 2020 states that the work described in that report (also performed under the WWFTP QA program) was assigned the technology level “Applied Research” and was conducted in accordance with procedure QA-NSLW-1102, *Scientific Investigation for Applied Research*. In both cases, all staff members contributing to the work received proper technical and QA training prior to performing quality-affecting work.

3.0 Background in Iodine Analytical Chemistry

Nearly all published radiochemical methods for trace ^{129}I analysis use an iodine carrier, typically 10 mg. The carrier is added to the starting sample, and then the iodine is separated from all other radionuclides using common methods such as precipitation, ion exchange, solvent extraction, and distillation. At the end of the separation, the iodine is precipitated as AgI or PdI_2, dried and weighed, then counted for ^{129}I gamma. The final weight of the AgI or PdI_2 is used to correct the counting data for chemical yield. Radioiodine can be measured very accurately this way, but the method cannot measure the chemical form of the trace iodine in the sample, and cannot measure stable iodine in the sample.

In the measurement of the chemical form of iodine in tank waste, no carrier can be used. The chemistry described in this report works on a sub-ppm scale. In this method, each inorganic chemical form of iodine is separated individually, in sequence, using solvent extractions and redox reactions. Iodine chemistry is fairly complex, and tank waste chemistry even more so. Tank waste has several oxidizing agents that could change the chemical form of the iodine during the analysis and cause iodine to show up in the wrong chemical form. The separations chemistry must be carefully chosen to avoid unintended redox reactions.

The chemistry will produce three fractions for each sample: free iodine, iodide, and iodate + periodate. The final chemical form of iodine in these three fractions will be iodide; the chemistry converts the starting iodine compound to iodide. The separated iodine (now in the form of iodide) is then measured by inductively coupled plasma mass spectrometry (ICP-MS). Both ^{127}I and ^{129}I are measured concurrently. In a tank waste, free iodine is expected to be zero, since I_2 reacts with strong bases. The iodate separation described in this report recovers periodate and iodate together, and their sum is reported.

Since the Hanford tank supernatants and solids have readily measurable iodine, detection limits are not a concern. A 0.2-mL sample of a typical tank waste will have several hundred nanograms of iodine, easy to measure with ICP-MS.

Iodide and iodate are commonly separated and measured by liquid chromatography followed by ICP-MS. A clean sample such as groundwater can be injected directly into the instrument and analyzed for iodine. Tank wastes, however, are messy, radioactive, saturated solutions of many compounds that precipitate aluminum hydroxide on dilution and form gases on acidification. Tank waste can be expected to quickly damage the chromatography column and alter the retention times after each injection. The wet chemical separations described in this report take longer than liquid chromatography, but will accommodate tank wastes, even using large sample sizes if necessary.

3.1 Brief Description of the Iodine Separations

Iodine, as the free element (I_2), readily extracts into carbon tetrachloride. Not much else extracts, and this is a convenient way to separate iodine in high purity from an aqueous sample. Iodide (I^-) can be extracted by first oxidizing it to I_2, then extracting it into CCl_4. Iodate and periodate (IO_3^- and IO_4^-) can be reduced to iodide, then oxidized to I_2 and extracted like the others. The extracted iodine in CCl_4 can be stripped back out of the CCl_4 with a mild reducing agent such as sodium sulfite solution.

The iodine separations used in this analytical method follow the general form shown below.

Free iodine separation: Measure the sample (typically 0.2 mL) into a glass centrifuge tube with 5 mL water and 5 mL CCl_4. The CCl_4 will extract free iodine out of the aqueous phase. Shake the tube for 5 minutes, then centrifuge to separate the phases. Draw off the CCl_4 layer (which has the iodine) and put it into a clean centrifuge tube. (Raw Hanford tank waste samples are not expected to have any free iodine, since free iodine would immediately convert to other chemical forms at the high pH of tank samples. Condensate samples or acidified tank waste may have free iodine.)

Iodide separation: Add 5 mL of clean CCl_4 to the first centrifuge tube (after free iodine has been removed). Acidify the sample and add a mild oxidizing agent, such as $NaNO_2$. The oxidizing agent will oxidize I^- to I_2, but will not affect IO_3^- or IO_4^-. Extract the I_2 (which represents iodide in the starting sample) into the CCl_4 as before, and centrifuge as before. Draw off the CCl_4 layer and put it into a second clean centrifuge tube.

(Iodate will react with iodide and form I_2 when the solution is acidified. However, the tank waste has approximately 10^5 times more nitrite than iodate, and the iodide-nitrite reaction should overwhelm the iodide-iodate reaction.)

Iodate separation: Add 5 mL of clean CCl_4 to the first centrifuge tube (after both free iodine and iodide have been removed). Chemically eliminate the nitrite with hydrogen peroxide, then add a reducing agent such as Na_2SO_3 and mix the solution. The reducing agent will reduce iodate to iodide. Then add an oxidizing agent ($NaNO_2$) to oxidize the iodide to I_2. Shake the tube for 5 minutes to extract the I_2 into the CCl_4. Centrifuge to separate the phases, then draw off the CCl_4 layer and put it into a third, clean tube.

At this point all of the inorganic iodine has been removed from the sample, and the sample can be discarded. The free iodine, iodide, and iodate from the sample have been separated and put into three fractions, in the chemical form of I_2 dissolved in CCl_4. But CCl_4 is unsuitable for injection into the ICP-MS, and the iodine must be back-extracted into aqueous solution before it can be measured.

Back-extraction: To each of the three centrifuge tubes, add a reducing agent such as Na_2SO_3 or N_2H_4 solution. Shake the tubes for a few minutes, then centrifuge the tubes to separate the phases. The iodine is now in the aqueous phase, no longer in the CCl_4. Draw off the aqueous phases and transfer them to clean, labeled vials.

Iodine measurement: Measure ^{127}I and ^{129}I in each of the three vials by ICP-MS. From the ICP-MS data, calculate the amount of iodine in each chemical form in the starting sample.

3.2 Elemental Iodine

The free element (I_2) is a volatile, crystalline black solid at room temperature. Its volatility must be kept in mind. In a closed jar, faint pink vapor can be seen above the black crystals. Just above room temperature, the solid evaporates to purple vapor. Iodine is slightly soluble in water and forms a pale brown solution. Iodine will evaporate slowly from solution, even at room temperature. (Iodine has a high solubility in aqueous iodide solutions, forming dark brown tri-iodide, but a high concentration of iodide will not normally be encountered in tank waste analysis. Formation of tri-iodide will not prevent evaporation of iodine.)

Iodine dissolves readily in many organic solvents. It forms a bright pink solution in carbon tetrachloride and chloroform. The pink color is discernable at 2 ppm in carbon tetrachloride and obviously pink at 10 ppm. Iodine will extract readily from aqueous solutions into carbon tetrachloride with a distribution coefficient of approximately 100. Iodine will also dissolve in polyethylene and polypropylene. Plastic transfer pipets will absorb iodine out of solution. Always use glass, not plastic.

The equilibration time for iodine to move to the carbon tetrachloride phase is several minutes with vigorous mixing. At an iodine concentration of 1 ppm, phase ratio of 10 aqueous to 1 carbon tetrachloride with continuous shaking by hand, the formation of pink color appears largely complete in 2 to 3 minutes. Two successive extractions of 5 minutes apiece using this phase ratio consistently gave essentially complete iodine recovery.

The equilibration time to strip iodine out of the carbon tetrachloride is much faster, complete in seconds with vigorous shaking. In many trials, 10 mL of 0.1M sodium sulfite was able to strip 200 µg of I_2 out of 50 mL carbon tetrachloride in 2-3 seconds with vigorous shaking.

3.3 Inorganic Forms of Iodine

The chemistry described in this and the following sections is well known and found in many reference books (e.g., Kolthoff and Sandell 1952; Mellor 1956). The remainder of this section shows what iodine compounds can be expected in tank waste and which redox reactions are most useful in iodine analysis.

The raw tank waste samples have a pH around 13. At this high pH, iodide, iodate, and periodate can coexist. Elemental iodine (I_2) will be absent because of its reaction with hydroxide. In neutral solution the I_2-water equilibrium [reaction (1)] lies far to the left, but in basic solution the reaction moves completely to the right, followed by disproportionation to iodate.

(1) $I_2 + H_2O \rightarrow HI + HIO$ (equilibrium is far to the left)

(2) $2NaOH + I_2 \rightarrow NaI + NaIO + H_2O$ (very fast; reversible)

(3) $3NaIO \rightarrow NaIO_3 + 2NaI$ (fast; basic conditions only)

Under acidic conditions, reaction (3) reverses, and iodide and iodate react to form iodine [reaction (4)]. The reverse reaction is stoichiometric and goes immediately to completion. This reaction will consume an exactly stoichiometric amount of H^+. Under acidic conditions, iodide and iodate cannot coexist in the same solution.

(4) $5HI + HIO_3 \rightarrow 3I_2 + 3H_2O$ (very fast; acidic conditions only)

Iodide reacts with iodine to form dark brown tri-iodide. The reaction is readily reversible.

(5) $NaI + I_2 \rightarrow NaI_3$ (equilibrium is far to the right)

Periodate is made by oxidizing iodate with a strong oxidizing agent such as chlorine or peroxydisulfate. Periodate will not normally form spontaneously from iodine in water, but it is easy to imagine that the soupy, intensely radioactive mixture in tank waste over several decades could form periodate. Periodate will generally react like iodate, and any periodate in a tank sample will report to the iodate fraction. In this report, periodate is not independently reported. The iodate fraction includes periodate.

3.4 Oxidation of Iodide

In dilute acid solution, nitrite ion will oxidize iodide ion to elemental iodine, which can be extracted into carbon tetrachloride or chloroform. This is a useful and well-known method to extract iodide ion. After the extraction, the excess nitrite may need to be eliminated to avoid interfering with the chemistry to follow. One reference recommends destroying the excess nitrite with urea or hydrazoic acid (Mellor 1956, p 945). Another recommends urea or sulfamic acid to destroy nitrite (Kolthoff and Elving 1961, vol 7, p 371). In this report, excess nitrite is eliminated with hydrogen peroxide.

(6) $HNO_2 + 2HI \rightarrow NO + H_2O + I_2$ (fast and complete at low pH)

At neutral and high pH, reaction (6) reverses, and iodine will slowly oxidize sodium nitrite to nitrate (7). This reaction may occur in raw tank waste, but not in an acidified sample undergoing iodine separations.

(7) $NaNO_2 + I_2 + H_2O \rightarrow NaNO_3 + 2HI$ (slow)

Hydrogen peroxide oxidizes iodide to elemental iodine under acidic conditions.

(8) $HI + H_2O_2 \rightarrow I_2 + 2H_2O$ (fast, acidic conditions only)

Many other oxidizing agents readily oxidize iodide to I_2 under acidic conditions. Some, such as chromate, are present in tank waste. Atmospheric oxygen will slowly oxidize iodide to iodine under acidic conditions. Iron(III) sulfate and iron(III) nitrate will slowly oxidize iodide to iodine in dilute acid.

An oxidizing agent that can convert I^- to I_2 under acidic conditions can also cause the formation of IO_3^-, because the I_2 (dissolved in water) will hydrolyze to HI and HIO, and the HIO will disproportionate to HIO_3 and HI. The oxidizing agent will continuously convert HI to I_2 and keep the system out of equilibrium so that IO_3^- can accumulate. Disproportionation of HIO to form IO_3^- is very fast in hot solution, but practically stops at 0°C.

3.5 Reduction of Iodine to Iodide

Iodine can be reduced to iodide with any of many reagents – bisulfite, hydroxylamine, hydrazine, Ti^{3+}, and many others. These reducing agents will strip iodine out of the carbon tetrachloride phase. Bisulfite reduces iodine at an acid concentration below about 50%. Above that acid concentration, the reaction reverses, and iodide ion reduces sulfate to sulfite or sulfide.

Sulfite reduces I_2 to I^-, forming sulfate. Sulfite is a fast and useful reagent for stripping iodine out of carbon tetrachloride.

(9) $I_2 + SO_3^{2-} + H_2O \rightarrow 2I^- + SO_4^{2-} + 2H^+$

Sulfite solution quickly reacts with atmospheric oxygen; it is ruined in a few hours of exposure to air. Sulfite will react with nitrite, ultimately reducing it to hydroxylamine (Jolly 1964, p 67). One nitrite takes up two sulfites [see reaction (10)]. In acid solution the first sulfite will readily hydrolyze and come off (as bisulfate). The second sulfite hydrolyzes much more slowly, leaving hydroxylamine. Since hydroxylamine will reduce iodate, the nitrite-bisulfite reaction will apparently not badly affect the iodine chemistry. PNNL has successfully used the redox sequence nitrite-sulfite-nitrite to sequentially measure iodide and iodate.

(10) $HNO_2 + 2HSO_3^- \rightarrow HON(SO_3)_2^{2-} + H_2O$ ($HON(SO_3)_2^{2-}$ is stable in alkaline solution)

(11) $HON(SO_3)_2^{2-} + H_2O \rightarrow HONHSO_3^- + HSO_4^-$ (fast in acidic conditions)

(12) $H^+ + HONHSO_3^- + H_2O \rightarrow NH_3OH^+ + HSO_4^-$ (0.5M HCl, boiling, 1 hour)

Hydroxylamine will reduce iodine to iodide under nearly neutral conditions (Mellor 1956, p 853).

(13) $4NaHCO_3 + 2I_2 + 2NH_2OH \rightarrow 4NaI + N_2O + 5H_2O + 4CO_2$

Hydrazine immediately reduces iodine to iodide at neutral pH [reaction (14)]. This is a useful method to back-extract iodine from carbon tetrachloride into aqueous solution. The solution must be neutral; if the aqueous solution is acidic, the reaction may not go to completion. Sodium sulfite accomplishes the same thing, but leaves sodium in the aqueous fraction, which can interfere with the ICP-MS iodine measurement.

(14) $N_2H_4 + 2I_2 \rightarrow N_2 + 4HI$

The classical iodometric titrations frequently use thiosulfate, and thiosulfate is mentioned extensively in the older literature. These reactions could be useful in tank waste analysis, but have not been tested in the work described in this report. Thiosulfate solution is stable in air, unlike sulfite solution. Under strongly alkaline conditions, iodine oxidizes thiosulfate to sulfate.

(15) $S_2O_3^{2-} + 4I_2 + 10OH^- \rightarrow 2SO_4^{2-} + 8I^- + 5H_2O$

In neutral or weakly alkaline solution, iodine oxidizes thiosulfate to tetrathionate.

(16) $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

3.6 Reduction of Iodate

Sulfite reduces iodate to iodide.

(17) $IO_3^- + 3SO_3^{2-} \rightarrow I^- + 3SO_4^{2-}$

Thiosulfate [reaction (18)] reduces iodate to iodide in acid solution. This is a commonly used standard method for titration of iodate. The reaction is quantitative, and can be used to standardize acids as well as iodate. However, sulfite also works well for this reaction, and PNNL has not tested thiosulfate for iodate reduction.

(18) $IO_3^- + 6H^+ + 6S_2O_3^{2-} \rightarrow I^- + 3S_4O_6^{2-} + 3H_2O$

Hydrazine reduces iodate to iodine. (One of the standard volumetric methods for hydrazine analysis is titration with iodate. Audrieth and Ogg 1951, p 159) The reaction is fast and stoichiometric in acid solution. Sulfite works just as well, however, and will work at a somewhat lower acid concentration than hydrazine. Reaction (19) shows reduction to iodine, but in practice (with excess hydrazine) the reaction will go all the way to iodide. Both sulfite and hydrazine carry the inconvenience of being readily oxidized by air.

(19) $4H^+ + 5N_2H_4 + 4IO_3^- \rightarrow 5N_2 + 2I_2 + 12H_2O$

One drawback is that hydrazine reacts with nitrous acid and nitrites to form hydrazoic acid in high yield, a potential hazard. Aqueous hydrazine does not react with dilute nitric acid. If hydrazine were used in iodine analysis, the quantity would be quite small, probably too small to create a hydrazoic acid hazard. But sulfite makes no hydrazoic acid at all.

An advantage of hydrazine is that it adds no dissolved solids to the solution. The ICP-MS can accommodate only a low concentration of dissolved solids, such as sodium.

Aqueous hydrazine is susceptible to air oxidation. The concentration may drop several percent per a day (Audrieth and Ogg 1951, p 154). Sodium sulfite solution is similarly sensitive to air oxidation.

None of these reducing agents under realistic conditions will stop at I_2. All the reducing agents will reduce iodate all the way to iodide. The iodide will need to be re-oxidized to I_2 before it can be extracted.

3.7 Tank Waste Composition

The tank wastes have several oxidizing agents that can alter the chemical form of iodine during analytical separations. These include nitrite, chromate, iron(III), and manganese(III-IV). Nitrite may be present at 1M or higher concentration, highly variable from tank to tank and far too high to ignore. Much less chromate than nitrite is generally present. The variability of the tank waste composition means that each tank sample must be accurately analyzed for nitrite so that the iodine chemistry can be kept in control. The primary interference is from nitrite, but chromate will also interfere if enough is present.

Part of the complexity of the iodine measurements is the complex chemistry of iodine, but part is also the complicated chemistry of nitrogen. The nitrogen anions in the tank wastes are nitrate and nitrite, oxidation states +5 and +3. When tank waste is acidified, the nitrite will protonate to free nitrous acid. Nitrous acid is not stable in dilute nitric acid solution and decomposes to NO and NO_2, oxidation states +2 and +4. This change in oxidation state indicates that disproportionation is occurring, which means redox reactions are taking place. Other components in the tank waste (such as iodine compounds) could participate in the nitrogen redox chemistry.

The nitrite concentration in a tank waste sample can be easily and accurately measured by titration with potassium permanganate. After the nitrite concentration has been accurately measured, the nitrite in a sample can be eliminated by adding an exactly stoichiometric amount of hydrogen peroxide. Hydrogen peroxide will convert nitrous acid to peroxynitrous acid, which will rearrange in a few minutes to nitric acid. Nitrite must be eliminated after the iodide separation, before the iodate separation. The hydrogen peroxide concentration must also be accurately known so that no excess hydrogen peroxide is added to a sample. Excess hydrogen peroxide would interfere with the iodate reduction to follow. The concentration of the hydrogen peroxide reagent can be accurately and quickly measured by potassium permanganate titration. If hydrogen peroxide is stored in a refrigerator, it will hold its concentration for several weeks.

Hydrogen peroxide will also reduce chromate to Cr(III) and eliminate its interference. If a tank has enough chromate to interfere with the iodine chemistry, it can be eliminated by reacting it with an equal number of moles of hydrogen peroxide. At room temperature, intensely blue peroxychromic acid will form, then decompose within about 30 seconds, leaving Cr(III). The exact chromate concentration would need to be known to avoid adding excess hydrogen peroxide, which could interfere with the chemistry to follow. This report does not have any provision for measuring chromate.

4.0 Measurement of Inorganic Iodine

4.1 Hazards

This work involves the radiological hazard of Hanford tank waste and the chemical hazard of carbon tetrachloride. The remaining hazards are those typical of radioanalytical chemistry – strong mineral acids, solid potassium permanganate and other chemicals, used in small quantities.

Tank waste samples are radioactive and must be handled in a radiological fume hood with lab coat, gloves, and safety glasses. The precautions taken for the radiological hazard will protect the analyst from the chemical hazards.

This iodine chemistry uses carbon tetrachloride or chloroform. Both are toxic, particularly carbon tetrachloride. Both are volatile and must be handled in a fume hood. Carbon tetrachloride will diffuse through latex and nitrile gloves. Do not spill carbon tetrachloride on gloves.

Hydrazine may be used. Hydrazine is toxic and chemically reactive.

4.2 Equipment and Reagents

Elemental iodine is volatile at room temperature and quite soluble in many organic compounds, including polyethylene and polypropylene. Any solution of elemental iodine must not be left open to room air, or some of the iodine will evaporate. Any equipment used to hold elemental iodine (including its solution in carbon tetrachloride or water) must be made of glass. Elemental iodine is chemically reactive and reacts with many metals, including stainless steel.

The labware should be leached before use to avoid isobaric interferences in the ICP-MS, particularly molybdenum. Typical leaching sequence is (1) warm laboratory detergent, (2) deionized water, (3) warm 0.5M nitric acid, (4) deionized water, and (5) dry at 105 °C.

The laboratory is expected to have common equipment such as beakers, volumetric flasks, vacuum filtration apparatus, a stirring hot plate, buret stand and 50-mL buret, and a centrifuge.

- Centrifuge tubes, 15-mL, glass, with screw caps (PNNL uses Pyrex 9826-16X)
- Centrifuge tubes, 15-mL, polypropylene, with screw caps (used to hold the final iodide solution before injection into the ICP-MS, not to hold an I_2 solution)
- Pipets, sizes ranging from 100 µL to 5 mL
- Glass Pasteur pipets, 5-mL capacity. Connect the end of the pipet to a 5-mL disposable syringe using Tygon tubing. (**Important:** Check to make sure the pipet will reach to the bottom of the 15-mL glass centrifuge tube. Some pipets are wider than the mouth of the centrifuge tube.)
- pH strips, pH range 0 to 14

Before preparing the reagents listed below, make sure no iodine is stored in the reagent cabinet. If the cabinet has a bottle of I_2, then don't use anything from that cabinet.

- Sodium nitrite solution ($NaNO_2$), 0.1M. Dissolve 0.690 g of solid $NaNO_2$ in 100 mL of water.

- Sodium sulfite (Na_2SO_3), 0.1M. Dissolve 0.252 g Na_2SO_3 in 20 mL of water. Sulfite solution oxidizes quickly in air and cannot be stored. Weigh the solid into a labeled 20-mL plastic vial, but do not add water until just before the sulfite solution is needed. Use the solution within a few hours.
- 0.010M tetramethylammonium hydroxide solution.
- Nitric acid, 0.5M. Other concentrations may be occasionally required.
- Hydrogen peroxide, 30%.
- Chloroform or carbon tetrachloride (either can be used). Do not use chloroform with any stabilizer or preservative.
- Potassium permanganate solution, 0.0100M. Weigh exactly 0.7902 g of solid potassium permanganate and dissolve in 500.0 mL of water. Filter it through a 0.45-µm polysulfone membrane filter on a plastic (not paper) support, to remove trace MnO_2. (The filter should show no more than a milligram or so of MnO_2. If not, then use a different source of $KMnO_4$.) Store the solution in a clean Teflon bottle. When a slight brown film (MnO_2) appears on the inside of the bottle, discard the solution and prepare fresh. (Remove all trace of the brown film before refilling the bottle with fresh $KMnO_4$ solution. The brown film can be removed from the empty bottle with strong hydrochloric acid. Rinse the bottle well with water to remove the hydrochloric acid.)
- Sulfuric acid, 0.1M. Add 5.6 mL of concentrated sulfuric acid to 1 liter of water.
- Oxalic acid 0.1M. Dissolve 9.004 g of oxalic acid in 100 mL of water.
- Hydrogen peroxide, 2M. Dilute 30% hydrogen peroxide approximately 1:5 with water. The actual peroxide concentration will be measured accurately by titration later. Store this solution in the refrigerator.

4.3 Notes on the Iodine Extraction.

In the chemistry to follow, iodine will be extracted out of aqueous solution and into carbon tetrachloride, in a glass centrifuge tube. The extraction is complete in several minutes with vigorous mixing. After extraction, the phases need to be separated. The easiest way to separate the phases is to draw one of the phases off with a glass Pasteur pipet. Carbon tetrachloride is dense and volatile and forms the lower layer. When carbon tetrachloride is removed from the centrifuge tube, its high vapor pressure may cause it to drip out the bottom of the pipet. The dripping can be avoided by previously filling the Pasteur pipet with carbon tetrachloride vapor. The Pasteur pipet is easiest to use if it is connected to a 5-mL disposable syringe with a short section of PVC tubing, such as Tygon. Do not allow liquid carbon tetrachloride into the Tygon tubing.

Run this chemistry in a fume hood known to be free of iodine contamination. The iodine blanks need to be low and reproducible. A high blank will cause scatter in the matrix spike yields, which increases the uncertainty in the reported data.

Make sure there is no bottle of iodine in the reagent storage cabinet. Iodine is volatile. If the cabinet has a bottle of iodine, then every reagent in the cabinet is probably contaminated with readily measurable iodine. If necessary, buy new reagents and store them in a clean location.

This iodine separation uses alternating oxidation and reduction, and the redox agents are critical. Each step must have enough oxidizing agent or reducing agent to eliminate what is left from the previous step, and still have enough to oxidize or reduce the iodine in the current step. If the procedure were to go off script (unexpected sample composition, bad pipetting, bad reagent, skipped procedure step), then too much of the wrong redox agent could be left in the sample, and the step would fail, and it probably wouldn't be obvious to the analyst.

The tank waste is radiologically hot. The iodine separations will eliminate nearly all of the beta activity, but the products will still have slight beta activity, probably measurable on a handheld Geiger-Mueller probe. If this beta activity is a problem for the ICP-MS, then the beta activity in the separated iodine fractions can be removed by passing the final solutions (in tetramethylammonium hydroxide solution, pH>7) through a small cation exchange column (0.5 mL of Bio Rad AG 50W-X8, 100-200 mesh, ammonium form). The cation column will not disturb the iodine, but will remove the cations (^{90}Sr, ^{137}Cs) and replace them with ammonium ion.

In a solvent extraction with carbon tetrachloride, the phases can be settled under gravity alone, but they will settle faster if they are centrifuged for a minute or two. A centrifuge will save time for the analyst and make the phase separation easier.

The mixing times for solvent extractions should be kept the same for all samples across all batches, so that the iodine recovery will be consistent from sample to sample and batch to batch. The prescribed mixing time (typically 5 minutes) is the minimum time judged to give essentially complete extraction of iodine in the carbon tetrachloride. Extending the extraction time risks allowing I_2 to inadvertently convert to unextractable HIO_3 (see the last paragraph of section 3.4). This unintentional conversion to HIO_3 is much faster above room temperature.

4.4 Iodide and Iodate Spike Preparation.

Prepare spike stock solutions with stable potassium iodide (KI) and potassium iodate (KIO_3) similar to the table shown below. Iodine is shown in the table, but no free iodine spike normally needs to be prepared. Weigh the reagents to four digits past the decimal and calculate the exact concentrations obtained.

			Parent Solution			Working Solution		
Chemical Form	Formula Weight		mass used (g)	dissolved in (mL)	ppm iodine	mL used	dissolved in (mL)	ppm iodine
I_2	253.81	g/mole	0.1000	100.0	1000.0	0.10	100.0	1.000
KI	166.00	g/mole	0.1308	100.0	999.9	0.10	100.0	1.000
KIO_3	214.00	g/mole	0.1686	100.0	999.8	0.10	100.0	1.000

When the tank waste analysis gets underway, make a matrix spike using a larger amount of stable iodine than the sample is expected to have so that the spike recoveries can be accurately known. PNNL has obtained good results with 1 μg stable iodine spike on top of 0.20 mL of tank waste. Reagent spikes should be occasionally included, perhaps every third or fourth batch. The reagent spikes will probably give a higher spike recovery than the samples since the samples have interferences not present in reagents alone. The reagent spikes will show the average recovery and reproducibility of the chemistry alone, and the matrix spikes will show the additional effect of interference from the particular tank sample under analysis.

The iodine measurement has no tracer. Any radiotracer can react with iodine already in the sample, possibly scrambling the chemical form and rendering the observed tracer yield meaningless. The yield must be monitored by matrix spikes in every sample processed. Each sample must be accompanied by an iodide matrix spike and an iodate matrix spike. Run the sample in triplicate, and run a reagent blank. If the blank is low and the triplicate results agree well, then the matrix spike yield will accurately reflect the triplicate sample yield. The tanks have widely variable composition and the yield from one tank will not necessarily reflect the yield from another.

Radiolabeled iodine spikes of accurately known concentration and accurately known chemical form are hard to prepare. Iodine-129 and I-131 are available, but their chemical form is not accurately known. We found one carrier-free lot of 2 mCi of ^{131}I marked and sold as NaI in dilute NaOH solution was a mixture of iodide and iodate. The stock may have been NaI at time of manufacture, but radiolysis converted part of it into iodate by the time it was used. We have found that oxidation of trace iodide to iodate is difficult and impractical if no residual oxidizing agent is to be left in solution.

4.5 Titration

Nitrite will interfere with the iodine separations, and nitrite is present at high concentration in Hanford tank waste. The nitrite concentration must be accurately measured before the iodine analysis gets underway. Nitrite is easy to measure by titration with potassium permanganate. Once reagents are prepared and the equipment is set up, each measurement takes only a few minutes.

Before beginning tank waste analysis, prepare 0.0100M potassium permanganate titrant, 0.1M sulfuric acid, and 0.1M oxalic acid. Use dilute sulfuric acid for the background solution. (The titrations consume H^+.)

In all of the titrations described below, use a large enough sample to consume at least about 20 mL of titrant. A 50-mL buret has a precision of ± 0.1 mL. At 20 mL, this is ± 0.5% uncertainty. But at 2 mL of titrant, the precision is ± 0.1 / 2.0 = 5% uncertainty, too much for the analysis.

Oxalate Titration. Use the oxalic acid as a daily titration check to show that the titration is in control.

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

Typical oxalic acid titration

10 mL 0.1M H_2SO_4 (1.0 mmole)

5.00 mL 0.1M $H_2C_2O_4$ (0.5 mmole)

Add several drops of $KMnO_4$ titrant, then warm the solution to near boiling (80°C). After the pink color clears (a few minutes), continue the titration. The titration should consume (2/5)(5.00 mL)(0.1M/0.01M) = 20 mL 0.0100M $KMnO_4$. When first setting up the titration, accurately measure the true oxalate concentration and write it on the bottle. All subsequent titrations should give the same oxalate concentration within a percent or two, demonstrating that the titration is in control.

Nitrite Titration. When a nitrite solution is acidified, HNO_2 forms, which slowly decomposes to NO and NO_2 gases. Decomposition is faster with warm, concentrated solution. To avoid a low bias, use the smallest practical sample volume and run the titration immediately after mixing, to avoid loss of NO and NO_2.

$$2KMnO_4 + 5NaNO_2 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5NaNO_3 + 3H_2O$$

Typical nitrite titration

10 mL 0.1M H_2SO_4 (1.0 mmole)

0.100 mL tank waste (approximately 2M nitrite, 0.2 mmole)

Titrate immediately, at room temperature, with good stirring. Toward the end of the titration, the endpoint will be slow. When the color takes 2 minutes to fade, call that the endpoint.

Hydrogen Peroxide Titration. The high concentration of hydrogen peroxide (2M) requires a 0.100M potassium permanganate solution, 10 times the concentration of the usual titrant. Weigh exactly 7.902 g $KMnO_4$, then dissolve it in 500.0 mL water. Filter it through a polysulfone membrane filter on a plastic support (not paper) to remove MnO_2, and store it in a Teflon bottle.

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5O_2 + 8H_2O$$

Typical hydrogen peroxide titration

40 mL 0.1M H_2SO_4 (8 mmole H^+)

2.00 mL 2M H_2O_2 (4 mmole)

Titrate at room temperature. The reaction requires an induction period of a few minutes. The approximate volume of titrant required is (2/5)(2.0 mL)(2.0M/0.1M) = 16 mL $KMnO_4$ titrant. Titrate carefully, in triplicate, to accurately measure the hydrogen peroxide concentration. Write the actual concentration on the hydrogen peroxide bottle. Store the hydrogen peroxide solution in a refrigerator.

Measurement of Nitrite in Tank Waste. The high nitrite concentration in tank wastes will interfere in the iodate measurement. The sample nitrite concentration must be accurately known so that later in the analysis it can be exactly oxidized to nitrate without altering the iodine speciation.

1. Set up a buret in a fume hood. Load it with 0.0100M potassium permanganate solution.
2. Add 10 mL of 0.1M sulfuric acid to the sample beaker. Measure 0.100 mL of tank waste into the beaker. Turn on the stirrer, and titrate the sample immediately. After titrating a sample, it can be tested for chromate (step 4), or thrown away. Don't save it for iodine speciation; all of its iodine has been oxidized to iodate.

To accurately titrate a high concentration of nitrite (such as tank waste), titrate a sample as described above to measure the approximate nitrite concentration, then titrate a second sample as follows: (1) add the usual volume of 0.1M H_2SO_4, (2) add 90% of the expected $KMnO_4$ titrant, (3) add the sample, and (4) turn on the stirrer and immediately titrate to the endpoint.

3. If the sample volume permits, run the titration in triplicate. The sample nitrite concentration needs to be known as accurately as practical. The triplicate analyses should have a standard deviation around 2% or less.
4. A titrated sample can be easily tested for chromate by adding 1 mL of 30% hydrogen peroxide. After the colored manganese compounds are killed by the peroxide (a few seconds), chromate will show up as blue peroxychromate, then fade after perhaps 30 seconds. The blue color is intense, but fades fast. If enough chromate is present, the final color will be pale lavender [Cr(III)].

4.6 Iodine Separation Procedure

Free Iodine Separation. The project may choose to skip the free iodine measurement. Because the raw tank wastes are strongly basic, it is unlikely that the samples have any measurable free iodine. Iodine immediately reacts with strong bases to form iodide and hypoiodite. The hypoiodite then quickly disproportionates into iodide and iodate.

1. Measure the raw sample (typically 0.2 mL) into a 15-mL glass centrifuge tube. Add 5 mL of water, then 5 mL of carbon tetrachloride. Cap the tube and mix it for 5 minutes.

2. Centrifuge the tube for a minute to separate the phases. Draw off the lower, carbon tetrachloride phase and put it into a clean, labeled centrifuge tube. Carefully avoid getting any of the aqueous phase, or suspended solids from the aqueous phase, into the carbon tetrachloride. Set the aqueous phase aside for step 6 below.

3. Add 1 mL of 0.1M sodium sulfite solution and 2-3 mL of water to the carbon tetrachloride. (Make the sodium sulfite solution immediately before use.) Cap the tube and mix it for 5 minutes. The sulfite solution will reduce I_2 to I^- and extract it back out of the carbon tetrachloride and into the aqueous layer.

4. Remove the (upper) aqueous layer and put it into a vial labeled for the free iodine measurement. Wash the carbon tetrachloride twice with 2-3 mL of water, and combine all the aqueous fractions. Discard the carbon tetrachloride.

5. Dilute the aqueous phase to 10.0 mL for ICP-MS analysis, using 0.01M tetramethylammonium hydroxide.

Iodide Separation. Iodide is separated from the diluted tank waste by oxidizing it to I_2 and extracting it into carbon tetrachloride. Native nitrite in the tank waste sample is used to oxidize iodide to iodine.

6. Use the aqueous sample from the free iodine measurement, or pipet 0.2 mL (accurately known) of tank waste into a 15-mL glass centrifuge tube and add 4.8 mL of water. The sample pH will be around 13.

7. Add 5 mL of carbon tetrachloride.

8. If the sample is not tank waste and has no nitrite, then add 1 mL of 0.1M sodium nitrite.

9. Add 1 mL of 0.5M nitric acid. Mix the solution, then use a pH strip to confirm that the solution is acidic.

   In a clean sample (such a condensate, but not tank waste), any iodide in the sample will react with iodate, forming iodine, $5HI + HIO_3 \rightarrow 3I_2 + 3H_2O$. If iodide is more than 5 times in excess of iodate, then iodate will be completely consumed. Excess iodate will not react; it will remain in solution. In a tank waste sample, nitrite is present at a concentration 10^5 times higher than iodine, and it will overwhelm the iodide-iodate reaction.

10. Shake the tube for 5 minutes.

11. Centrifuge the tube to separate the phases. Draw off the carbon tetrachloride and put it into a clean 15-mL centrifuge tube. Avoid getting ANY of the aqueous phase. (Set the aqueous phase aside for step 15.)

12. To the carbon tetrachloride in the clean tube, add 2-3 mL water and 1 mL of 0.1M sodium sulfite. Mix the tube for 5 minutes, then centrifuge to separate the phases.

13. Draw off the aqueous (upper) layer and put it into a clean container labeled for the iodide fraction. Wash the carbon tetrachloride twice with 2-3 mL of water apiece, and collect all the aqueous solution together.

14. Adjust the volume of the aqueous phase to 10.0 mL with 0.01M tetramethylammonium hydroxide.

Iodate Separation. The sample, with free iodine and iodide removed, is in acidic aqueous solution in a glass centrifuge tube from step 11 above. The sample still has nitrite and chromate, which are oxidizing agents and will interfere in the iodate reduction.

15. To the sample solution in its glass centrifuge tube, add 5 mL of clean carbon tetrachloride.

16. Calculate the exact number of millimoles of nitrite in the sample aliquot. Calculate the volume of 2M hydrogen peroxide needed for that exact number of millimoles (millimoles nitrite = millimoles peroxide). The peroxide can be in slight excess, but not enough excess to kill all of the sulfite in step 17, coming up. Excess peroxide will react with chromate in the sample.

    Add exactly that amount of hydrogen peroxide. Mix the solution, then give it 10 minutes for the reaction to go to completion.

    At this point, the nitrite is gone, oxidized to nitrate by the hydrogen peroxide. Chromate is probably also gone, reduced to Cr(III) by the hydrogen peroxide.

17. Add 1 mL of 0.1M sodium sulfite solution and mix the solution. The sulfite, in acidic sample solution, will reduce iodate to iodide. Let the samples stand for approximately 5 minutes for the reduction to occur.

18. Add 1 mL of 0.1M sodium nitrite. Cap the tube immediately. The nitrite will react with and eliminate the sulfite, then re-oxidize the iodide to I_2, which will extract completely into the carbon tetrachloride. (One mole of nitrite reacts with two moles of sulfite, so that nitrite is left in excess.)

19. Mix the tube for 5 minutes.

20. Centrifuge the solution to separate the phases, then draw off the carbon tetrachloride with a glass Pasteur pipet. Put the carbon tetrachloride into a clean glass tube.

21. Add 2 mL of clean carbon tetrachloride to the aqueous phase. Mix it for 5 minutes, then centrifuge to separate the phases. Draw off the carbon tetrachloride and combine it with the previous 5 mL of carbon tetrachloride.

22. To the carbon tetrachloride, add 1 mL of 0.1M sodium sulfite and 2-3 mL water. The sulfite will reduce I_2 to I^- and strip it out of the carbon tetrachloride. Mix the solution for 5 minutes.

23. Centrifuge the tube to separate the phases. Pull off the aqueous layer and put it into a clean, labeled tube. (Can be 15-mL polypropylene tubes.) Wash the carbon tetrachloride twice with 2-3 mL of water apiece, and combine all the aqueous phases.

24. Dilute the aqueous phase to 10.0 mL with 0.01M tetramethylammonium hydroxide.

    Label the vials accurately, then take the vials to the ICP-MS lab. A large number of fractions will result from the analysis of just one tank. Each tank sample consists of a set of six analyses:
    - Sample, duplicate sample, triplicate sample
    - Iodide matrix spike
    - Iodate matrix spike
    - Blank

    Each one of the six analyses makes three fractions for ICP-MS measurement: Free iodine, iodide, and iodate fractions. Therefore,

    (6 analyses)(3 fractions per analysis) = 18 vials (iodine fractions) for the ICP-MS. Make the labels obvious.

4.7 Iodine Measurement by ICP-MS

Report masses 127 and 129. The ICP-MS must have some provision for handling xenon interference in the argon plasma. Molybdenum also causes an isobaric interference (from molybdenum oxides). Molybdenum interference must be controlled by carefully cleaning the glassware before use and using good grade reagents.

The raw ICP-MS data should not be censored by substituting “<EQL” for the actual result below the estimated quantitation limit (EQL). Instead, every data point needs to be reported as measured, whether or not it is below the EQL. Many data points will be below the EQL, and some will be below the instrument detection limit, since not all chemical forms of iodine will be present in every sample.

It is important to report negative results. All measurements have uncertainty. If the blank is truly zero, then half the blank data will be slightly negative and half slightly positive, so that they average zero with a large standard deviation. If negative results are removed from the data set, then the blanks will falsely average a positive result and the standard deviation will be wrong.

The data evaluation will be easier if the ICP-MS reports actual data with an uncertainty estimate for each measurement. Below the EQL, the uncertainty will be larger. At or below the instrument detection limit, the uncertainty may be larger than the result.

The total uncertainty will be known from the standard deviation of the triplicate results for each sample. If the instrument uncertainty is known, then the uncertainty in the chemistry can be calculated.

5.0 Calculations

Tabulate the raw ICP-MS data and make dilution corrections. Calculate the mass of ^{127}I and ^{129}I in each sample fraction. If the ICP-MS reported an uncertainty, then include the instrument uncertainty for each measurement.

If the instrument did not report uncertainty with each result, then an instrument uncertainty can be estimated as a linear function of the result. Assume ± 100% at the instrument detection limit, and much smaller uncertainty (judged by the standard deviation of the continuing calibration standards, say, ± 5%) at the EQL, with a linear fit in between. Above the EQL, use a constant ± 5% (or whatever uncertainty is judged to be appropriate above the EQL).

The triplicate samples should agree reasonably well, ideally only a few percent larger than the instrument uncertainty. The uncertainty in the chemistry is the difference between the total uncertainty (standard deviation of the triplicates) and the instrument uncertainty. (Remember that uncertainties from uncorrelated sources add in quadrature.) The blank should be small compared to the samples, so that the blank correction is small. (High blanks can have a large effect on the matrix spike yields, which is then propagated through the sample results.)

Calculate the spike yields after the blank correction has been made. The chemistry does not include enough washes to give 100% iodine recovery, but the recovery should be consistent since all volumes were measured with pipets and all mixing times were the same. The reagent spikes will probably have a higher recovery than the matrix spikes. The blanks should be small compared to the spikes.

If the triplicate sample results agree well, then the analysis is shown to be reproducible and the matrix spike yields are probably accurate. The matrix spike yields may be lower than generally encountered in radiochemistry (40%), but they are valid if the analysis is reproducible.

Correct the sample results for the matrix spike recovery.

For each sample, calculate free iodine, iodide, and iodate, for both ^{127}I and ^{129}I. If the chemistry worked, then free iodine will be essentially zero for tank samples. For non-tank samples (such as acidic condensates), it may be necessary to report free iodine.

Total ^{129}I has been analyzed and published for most tanks. Compare the new data to previously measured data. The two numbers will probably not agree exactly, since the tanks are not homogeneous, but they should agree reasonably well.

After several batches of data have been accumulated, combine the data into one set. The blanks should be consistent, with no fliers. The matrix spike recoveries should not be wildly different from one tank to the next, although each tank may have unique interferences.

6.0 Conclusions

This report summarizes the measurement of the inorganic chemical forms of iodine in Hanford tank waste. The Hanford tank wastes have roughly 1 part per million iodine. Part of the iodine is the long-lived beta emitter ^{129}I, and the rest is stable ^{127}I. Because tank waste iodine is radioactive and radiotoxic, its chemical form must be known so that its behavior in the vitrification process can be reliably known and anticipated in various waste streams (glass, secondary liquid and solid waste, and offgas emissions) at Hanford.

Iodine in tank wastes exists in the inorganic chemical forms iodide and iodate (and possibly also periodate) and also as organic forms such as alkyl iodides. The measurement of organic iodides is very different from the measurement of inorganic forms and is outside the scope of this report.

The inorganic chemical forms are chemically separated, in sequence, from the raw tank waste using solvent extractions and several redox reactions, then measured by ICP-MS. The inorganic chemical forms of iodine are chemically reactive, and so is the tank waste. The chemistry must be carefully designed to avoid unintended reactions that could convert one form of iodine to another during the analysis, which would skew the data and report iodine in the wrong chemical form. This iodine analysis, developed at PNNL, is being transferred to the DOE 222-S Laboratory on the Hanford Site, in Washington State, for implementation during waste processing operations.

7.0 References

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