Pacific Northwest
NATIONAL LABORATORY

PNNL- 35134

Control of iodine and tellurium for use in domestic molybdenum-99 production efforts

September 2023

Leah M Arrigo
Matthew A D RisenHuber
Ean S Arnold
Kirby P Hobbs
Kurt Silvers
Nicolas Uhnak

U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

DISCLAIMER

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from
the Office of Scientific and Technical Information,
P.O. Box 62, Oak Ridge, TN 37831-0062
www.osti.gov
ph: (865) 576-8401
fox: (865) 576-5728
email: reports@osti.gov

Available to the public from the National Technical Information Service
5301 Shawnee Rd., Alexandria, VA 22312
ph: (800) 553-NTIS (6847)
or (703) 605-6000
email: info@ntis.gov
Online ordering: http://www.ntis.gov

PNNL- 35134

Control of iodine and tellurium for use in domestic molybdenum-99 production efforts

September 2023

Leah M Arrigo
Matthew A D RisenHuber
Ean S Arnold
Kirby P Hobbs
Kurt Silvers
Nicolas Uhnak

Prepared for
the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory
Richland, Washington 99354

Summary

Three initial proof-of-concept experiments were performed to test the removal of I and Te from solutions containing Mo for potential abatement during chemical processing to purify ^{99}Mo. All three proof-of-concept experiments produced results indicating that further optimization could provide methods for I and/or Te abatement from multiple matrices.

Decamp and Happel (2013) describe the use of CL resin from Eichrom Technologies loaded with Ag^+ combined with Amberlite XAD-4 in the chromatographic separation of irradiated fission products in 1 M HNO_3 to separate iodine species where iodide and iodate react with Ag^+ and I_2 adheres to the Amberlite resin. The method worked well under processing conditions in a medical isotope facility although many separation methods use higher concentrations of HNO_3 which could adversely impact the Ag^+ loading. The experiment performed here used a roughly 2 mL column of CL resin loaded with Ag^+ and Amberlite XAD-4 to separate µg quantities of I, Te, and Mo in 3 M HNO_3. The results indicate Te is not in the optimal oxidation state and did not adhere to the column, Mo does not adhere to the column, and the separation of iodine could not be determined due to issues with yielding stable iodine species using ICP-MS. The Ag elution was extremely low showing the column separation is not impacted using 3 M HNO_3 under the conditions tested and an optimized method might be suitable for iodine abatement. The use of a redox reagent would be needed to use the method for Te abatement, however this a difficult prospect in HNO_3.

Like Ag^+, some I and Te species react with Pb^{2+}, therefore Pb^{2+}could be implemented in a similar chromatography separation to CL resin loaded with Ag^+. SR resin available from Eichrom Technologies sorbs Pb^{2+} strongly in 0.1-10 M HNO_3 so this was chosen for the separation. The separation of a solution of I, Te, and Mo in 3 M HNO_3 using SR resin loaded with Pb^{2+} resulted in the formation of PbI_2 on the column as desired, little to no Te reacted with the Pb^{2+} indicating Te is not in the optimal oxidation state, and little to no Mo sorbed to the column as desired. The results indicate this method could be used in the removal of I from the solution with optimization of the chromatography parameters. The use of a redox reagent to adjust the Te oxidation state would be required to use this method for Te removal.

Iodine and Te species also react with Sn^{2+} to produce a precipitate which can be filtered to separate I and Te from Mo; in the case of Te, Te metal is formed. Solutions of I, Te, and Mo in H_2SO_4 were contacted with 5% $SnCl_2$ in H_2SO_4 followed by filtration. The results showed removal of a significant portion of Te and some removal of Mo. Maximizing the removal of Te while minimizing the Mo loss requires further optimization of the method. The experiments did show this could be a way to separate Te and Mo although there were issues with yielding I from an acidic solution which would need to be addressed. It should be noted that this method is not compatible with an oxidizing system like HNO_3 since this will dissolve the Te metal formed. A neutral or reducing acid matrix like HCl or H_2SO_4 is required.

Acknowledgments

This work was performed as part of the National Nuclear Security Administration's cooperative agreements for the production of ^{99}Mo. The authors would like to thank Caleb Allen for performing the gamma energy analysis using HPGe.

Acronyms and Abbreviations

µg	Microgram
µm	Micrometer
Bq	Becquerel
cm	Centimeter
DI	Deionized
FP	Fission Product
g	Gram
H_2BP	Butyl Dihydrogen Phosphate
HDBP	Dibutyl Hydrogen Phosphate
HDEHP	Di(2-ethylhexyl) Phosphoric Acid
HEU	Highly Enriched Uranium
HPGe	High Purity Germanium
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectroscopy
ID	Inner Diameter
IRE	National Institute for Radioelements
K	Equilibrium constant written in terms of activity ratios
M	Molality (moles / kilogram solvent)
M	Molarity (moles / liter solvent)
mg	Milligram
mL	Milliliter
NA-231	National Nuclear Security Administration, Office of Conversion
NNSA	National Nuclear Security Administration
pH	Negative base-10 logarithm of the H^+ ion concentration (or activity)
PNNL	Pacific Northwest National Laboratory
Redox	Reduction-Oxidation
TBAB	Tetrabutyl Ammonium Bromide
TBP	Tributyl Phosphate
UREX	Uranium Extraction
UNF	Used Nuclear Fuel

Contents

Figures

Tables

1.0 Introduction

As ^{99}Mo is an important diagnostic tool in the world of medicine, the National Nuclear Security Administration (NNSA) Office of Conversion (NA-231) has been assisting potential domestic producers in standing up their technologies. They have also been helping in designing systems that do not use highly enriched uranium (HEU). Pacific Northwest National Laboratory (PNNL) has been assisting in the capture and sequestering of certain volatile radionuclides, e.g., I, Xe, that are inherently produced during the process of nuclear fission by ^{235}U and that need to be kept below certain regulatory standards. Failure to capture these isotopes expose plant workers as well as the general public to harmful radiation, especially in the case of I, which bioaccumulates in the thyroid. This report provides an overview of research that PNNL has performed in the last year exploring the possibility of sequestering Te and I before separating ^{99}Mo. A short overview of Te and I chemistry is included before the experimental work and discussion.

2.0 The Chemistry of Iodine

The production of ^{99}Mo is most often achieved through the irradiation of uranium targets such as U_3O_8 to induce fission using a number of methods such as using neutron or gamma induced fission. A wide variety of fission products (FPs) are produced during the irradiation including ^{99}Mo and a variety of iodine and tellurium isotopes including ^{129}I, ^{131}I/Te, ^{132}I/Te, and ^{133}I. When the targets are dissolved in an acidic matrix such as nitric acid (HNO_3), a large fraction (greater than 90%) of the iodine may be released as vapor. Therefore, abatement of radioiodine emissions depends on understanding how much iodine vapor is formed and designing a system to remove it from the off gas. The following section presents a review of iodine chemistry and capture methods. A review of tellurium chemistry and capture methods is included in section 3.0.

2.1 Iodine Speciation

Iodine speciation is quite complex and dependent on a range of variables including iodine concentration, temperature, pH, matrix composition, and the presence of reduction-oxidation (redox) active species including metals such as Ce, Cu, and Cr as well as sulfite, peroxides, etc.

2.1.1 Iodine Concentration

Iodine speciation is dependent on the iodine concentration, which impacts the reaction kinetics as well as the redox characteristics. I_2 formation will occur at a faster rate at higher iodine concentrations due to an increased likelihood the iodine atoms will interact with one another; this probability decreases as the iodine concentration decreases. In low concentration the equilibrium is shifted to favor non-molecular species, while increasing the concentration of total iodine will shift the species towards higher molecular species such as I_2 and I_3^-. The pertinent equations and expressions for the formation of molecular iodine species are shown in **Error! Reference source not found.** through Equation 2-6.

$$2I^- \leftrightarrow I \qquad \text{Equation 2-1}$$

$$I^- + I_2 \leftrightarrow I_3^- \qquad \text{Equation 2-2}$$

$$K_1 = \frac{[I_2]}{[I^-]^2} \qquad \text{Equation 2-3}$$

$$K_2 = \frac{[I_3^-]}{[I^-][I_2]} \qquad \text{Equation 2-4}$$

$$rate\ of\ I_2\ formation = k_f[I^-]^2 - k_r[I_2] \qquad \text{Equation 2-5}$$

$$rate\ of\ I_3^-\ formation = k_f[I^-][I_2] - k_r[I_3^-] \qquad \text{Equation 2-6}$$

In addition, in solutions with low concentrations of I_2, I_2 is both a better oxidizing and a better reducing agent than when I_2 is present at higher concentrations. If comparing aqueous solutions at pH 7 containing 10^{-3} and 10^{-7} M of I_2 with the following reaction equilibria:

$$I_{2(aq)} + H_2O \leftrightarrow H^+ + I^- + HIO \qquad K = 3x10^{-13}$$ Equation 2-7

- 10^{-3} M I_2: 8% of I_2 is hydrolyzed to HIO
- 10^{-7} M I_2: 98% of I_2 is hydrolyzed to HIO

When the solution contains 10^{-3} M I_2, I_2 is very stable and HIO is highly unstable but reducing the I_2 concentration to 10^{-7} M alters the equilibria such that I_2 is highly unstable and HIO is somewhat stable (Kahn and Kleinberg 1977).

2.1.2 Redox Reactions and Reaction Kinetics

Iodine speciation is affected by reaction kinetics. General reaction rates and the iodine speciation are provided in Table 2-1, Table 2-2, and Table 2-3 for a variety of iodine reactions in different solutions with or without the addition of redox reagents. One thing to note is that while the addition of the redox reagents listed in Table 2-3 will promote formation of I_2, they could possibly affect downstream chemistry.

Table 2-1. Redox reaction rates for iodine solutions at room temperature (Kahn and Kleinberg 1977)

Reaction	Description of Rates
$5\ I^- + IO_3^- + 6\ H^+ \leftrightarrow 3\ I_2 + 3\ H_2O$	Rapid in acidic solution
$I^- + I_2 \leftrightarrow I_3^-$	Rapid and reversible; K = 768 at 25°C
I_2 (aq) + $H_2O \leftrightarrow I^- + HIO + H^+$	Fairly rapid; $K = 5.4x10^{-13}$ at 25°C
$3\ IO^- \leftrightarrow 2\ I^- + IO_3^-$	Very rapid at pH greater than 8

Table 2-2. Redox reaction rates for iodine in oxidizing solution at room temperature (Kahn and Kleinberg 1977)

Reaction	Description of Rates
$4\ I^- + O_2 + 4\ H^+ \leftrightarrow 2\ I_2 + 2\ H_2O$	Slow in low concentrations of H^+; the rate is increased in high concentrations of H^+; the reaction is induced by light and various ions
$2\ I^- + 2\ H^+ + H_2O_2 \leftrightarrow I_2 + 2\ H_2O$	Moderately rapid in 0.1 M H^+ ion; hastened by molybdate

Table 2-3. Redox reaction rates for iodine in solutions containing metal-based redox reagents at room temperature (Kahn and Kleinberg 1977)

Reaction	Description of Rates
$2\ I^- + 2\ Ce^{4+} \leftrightarrow I_2 + 2\ Ce^{3+}$	Rapid in acidic solution
$2\ I^- + 2\ Fe^{3+} \leftrightarrow I_2 + 2\ Fe^{2+}$	Reversible and moderately rapid in acidic solutions; equilibrium is established in several minutes
$4\ I^- + 2\ Cu^{2+} \leftrightarrow I_2 + 2\ CuI$	Quantitative and rapid
$6\ I^- + Cr_2O_7^{2-} + 14\ H^+ \leftrightarrow 3\ I_2 + 2\ Cr^{3+} + 7\ H_2O$	Very slow at low concentrations of H^+ ion. Moderately rapid in 0.3 M H^+ ion; the reaction is complete in about 5 minutes.
$I_2 + Sn^{2+} \leftrightarrow 2\ I^- + Sn^{4+}$	Rapid
$2\ I_2 + As_2O_3^{2-} + 5\ H_2O \leftrightarrow 4\ I^- + 2\ H_3AsO_4 + 4\ H^+$	Completely reversible; at pH between 9 and about 4, the reaction proceeds to the right rapidly; in

Reaction	Description of Rates
	strongly acidic medium the reaction goes from right to left.
$2\ IO_3^- + As_4O_6 + 2\ Cl^- + 4\ H^+ \leftrightarrow 2\ ICl + As_4O_{10} + 2\ H_2O$	Reaction is quantitative when the molarity of HCl is 3 or greater

In fission solutions, redox reagents are always present through the radiolysis of the solutions, whether that is the water or the electrolyte. The solvent, water, is the primary target of radiolysis in solutions <0.5 M, beyond that concentration of radiolysis occurs on the electrolyte. (Choppin) The primary water radiolysis products are shown in the Table 2-4, with their associated reduction potentials. In solution the radiolysis products will react with anything in solution causing some redox reactions to occur.

Table 2-4. Select radiolysis product G-Values in µmol/J from water. G-values in parentheses are reported in molecules/100 eV.

Product	G-value (pH 3-11)[a]	G-value (pH 0.5)[a]	Reduction potential (vs NHE)
e^-_{aq}	0.280 (2.70)	0 (0)	-2.9 V[a]
·OH	0.280 (2.70)	0.300 (2.90)	2.7 V[a]
·H	0.060 (0.58)	0.380 (3.65)	-2.3 V[a]
H_2	0.047 (0.45)	0.041 (0.40)	0 V
H_2O_2	0.073(0.70)	0.0081 (0.078)	1.35 V[b]
HO_2·	0.0027 (0.026)	0.00080 (0.0077)	1.05 V[b]
H^+	0.321 (3.10)	-	

[a] Values obtained from Caer 2011
[b] Values obtained from Koppenol, Stanburry, and Bounds 2010
[c] Values obtained from Pastina & LaVerne (2001)

2.1.3 Iodine in Acidic Solutions

Iodine speciation is dependent on the solution pH as well as matrix concentration. In 3 M HNO_3, the most stable forms of iodine are I_2 and IO_3^-. These iodine species will be in equilibria with other iodine forms including I^- and IO_4^-. I_2 is volatile and is soluble in organic solvents, while I^-, IO_3^-, and IO_4^- are not. It is possible to favor the formation of I_2 by increasing the iodine concentration, altering the solution acidity, adding redox reagents, and/or heating the solution. Increasing the solution temperature will increase I_2 volatilization, which will drive further formation of I_2 until the iodine concentration is a limiting factor. It is important to note that I_2 is a solid at room temperature and will solidify on any cool surfaces, so it may be necessary to warm any surfaces where I_2 is not desired (Kahn and Kleinberg 1977).

Iodine speciation has been studied for the processing of used nuclear fuel (UNF). When UNF is dissolved in 3–10 M HNO_3 at 100°C, 1–6% of the iodine remains in solution while 94–99% is volatilized. The vapor phase generated during the dissolution is water-saturated air containing roughly 22 parts per million (ppm) by mass I_2, 10,000 ppm NO_x, and 10 ppm Cl_2. In addition to I_2, HI, HOI, and some organic iodides such as CH_3 and C_2H_5I form; not all organic iodides will volatilize. The iodine speciation has been shown to be affected by pretreating the SNF with high-temperature air, oxygen, or NO_x. The presence of NO_2 has been shown to affect the speciation of iodine, and bubbling NO_2 through the dissolver solution can minimize the formation of insoluble colloids with fission products like Pd and Ag (Riley 2016). The presence of HOI,

hypoiodidic acid, or hydroiodic acid, can be minimized by minimizing the gaseous moisture content (Borisov 2004).

2.1.4 Iodine in Alkaline Solutions

In alkaline solutions, I_2 is converted primarily to I^- and IO_3^- as shown in Equation 2-8. Alkaline or caustic scrubbing, also referred to as wet scrubbing, can be used to convert I_2 to nonvolatile species, which remain in the alkaline solution; this method does not remove any organic iodine species such as CH_3I (Kahn and Kleinberg 1977).

$$3\,I_2 + 6\,OH^- \leftrightarrow 5\,I^- + IO_3^- + 3\,H_2O \qquad \text{Equation 2-8}$$

2.1.5 Colloid Formation with Fission Products

Iodine forms highly insoluble precipitates with elements such as Ag and Pd. Ag and Pd are low-yield FPs, so it is possible for colloidal AgI and PdI to form in solutions of irradiated U. Formation of the colloids prevents separation of iodine through I_2 volatilization or solvent extraction as well as separation of I^- or IO_3^- through separation techniques such as ion exchange chromatography. Sakurai et al. (1997) performed a set of experiments looking at the iodine speciation in HNO_3 solutions containing U with or without FPs; the solutions were formulated to correspond to used fuel with a burnup of 40 gigawatt-day/ton (GWD/t) U. The solutions were heated at 100°C for 3 hours after which the amount of iodine remaining in the solution and the iodine speciation were determined. The amount of volatile and nonvolatile iodine for each run are shown in Table 2-5 and the amounts of various species of nonvolatile iodine (I_2, I^-, IO_3^-, organic iodide, and colloidal iodide) are shown in Table 2-6. Based on these results, Sakurai et al. were able to determine that the formation of colloidal iodine can be avoided under the conditions tested by maintaining an iodine concentration of less than 0.7 µg I/100 mL corresponding to 5.52×10^{-5} M I; irradiated U with a lower burnup will contain fewer Ag and Pd FPs, which would permit a higher concentration of iodine before colloid formation would be a concern (Sakurai et al. 1997). Colloid formation can be minimized by bubbling NO_2 through the nitrate solution (Sakurai et al. 1997; Riley et al. 2016).

Table 2-5. Quantity of volatile and nonvolatile iodine present in mock used fuel samples with a burnup of 40 GWD/t U under multiple experimental conditions (Sakurai et al. 1997)

Run	HNO_3 (M)	Uranium (g U/L)	N_2 Flow (30 mL/min)	NO_2 in N_2 (%)	Starting KI (µg)	Volatile Iodine (%)	Iodine in Solution (%)
1	3.4	50 (**no FP**)	Bubbling	0	1000	91.9%	8.1%
2	3.4	50	Bubbling	0	1000	96.4%	3.6%
3	3.4	50	Bubbling	10	1000	98.5%	1.5%
4	3.4	50	Sweep	0	1000	93.3%	6.7%
5	3.4	250	Bubbling	0	1000	94.8%	5.2%
6	6.1	50	Bubbling	0	1000	61.0%	39.0%
7	6.1	50	Bubbling	10	1000	95.6%	4.5%

Table 2-6. Quantity of various nonvolatile iodine species present in mock used fuel samples with a burnup of 40 GWD/t U under multiple experimental conditions (Sakurai et al. 1997)

					Percent of Nonvolatile Iodine				
Run	HNO_3 (M)	Uranium (g U/L)	N_2 Flow (30 mL/min)	NO_2 in N_2 (%)	I_2 in Solution	I^- in Solution	IO_3^- in Solution	Organic Iodide	Colloidal Iodide

1	3.4	50 (**no FP**)	Bubbling	0	17.8%	1.7%	81.0%	1.0%	1.4%
2	3.4	50	Bubbling	0	13.1%	4.5%	48.6%	7.8%	18.2%
3	3.4	50	Bubbling	10	20.7%	4.7%	16.7%	11.3%	59.3%
4	3.4	50	Sweep	0	15.0%	2.5%	24.2%	5.3%	42.3%
5	3.4	250	Bubbling	0	22.2%	1.9%	13.0%	3.9%	37.7%
6	6.1	50	Bubbling	0	10.6%	1.7%	53.4%	2.8%	1.5%
7	6.1	50	Bubbling	10	13.7%	4.5%	55.7%	8.3%	9.2%

2.2 Iodine Capture

Iodine can be captured in a variety of ways using the different iodine species under different experimental conditions. Capture methods include using a cold trap to cool I_2 from a gas into a solid, wet capture, and adsorbent processes.

Wet capture includes a variety of methods including alkaline scrubbing, the Mercurex process, the Iodox process, molten hydroxide, electrolytic scrubbing, fluorocarbon absorption, and silicon-organic solvent. Of these methods only the alkaline scrubbing method is discussed here; the other methods have prohibitive safety concerns and/or high costs (Nandanwar et al. 2016).

Compared to wet capture, adsorbent processes are simple and reliable and have low operating and maintenance costs. Sorbent materials typically considered for use in iodine capture include activated carbon (AC) and silver exchanges or impregnated sorbets such as alumina, silica, and zeolites. The primary challenges to using adsorbent processes are the effectiveness of the sorbent and the sorbent cost (Trevorrow et al.1983; Kang et al. 2020; Huve et al. 2018; Nandanwar et al. 2016).

2.2.1 Cold Trap

Gaseous I_2 will solidify on cool surfaces, so it is possible to use a cold trap to collect I_2 following volatilization. I_2 can be collected with any other gases present such as N_2, Kr, Xe, etc. using a cold trap at a temperature low enough to liquify or solidify all the gaseous species. I_2 condenses into a solid at a much higher temperatures than those at which gaseous species like N_2, Kr, Xe, etc. will liquify and can be separated from the gases using a cold trap at an appropriate temperature.

2.2.2 Alkaline Trap

I_2 is removed from a sample using an alkaline trap by bubbling a carrier gas such as air, N_2, or Ar through the sample solution, which is then bubbled through the alkaline solution. Used fuel reprocessing plants typically use alkaline traps containing solutions of 1–2 M NaOH, which have a maximum efficiency of 90% and a typical decontamination factor of 10–100 (Kahn and Kleinberg 1977; Haefner and Tranter 2007; Trevorrow et al. 1983; Riley et al. 2016). It should also be noted that since I_2 solidifies on cool surfaces, I_2 loss can be minimized by warming any tubing or other surfaces between the sample solution and the alkaline trap.

The effectiveness of the alkaline trap is dependent on several variables including the alkaline solution volume, the hydroxide concentration, the carrier gas flow rate, and the gas bubble size. These variables can be optimized to maximize the gas resident time and solution contact time to maximize the iodine recovery. More than one alkaline trap can be set up in series to increase the solution volume without increasing the overall size of the trap.

The alkaline trap will also react with CO_2 and NO_x gases. Reaction of NO_x gases with the alkaline solution will affect the hydroxide concentration, which may require correction with the addition of hydroxide, altering the initial hydroxide concentration to accommodate for the loss, use of a larger solution volume, etc. If the gas stream contains a significant amount of CO_2 it is possible to precipitate Na_2CO_3; this problem can be avoided by using KOH rather than NaOH because the solubility of K_2CO_3 is higher than that of Na_2CO_3 (Kahn and Kleinberg 1977; Haefner and Tranter 2007; Trevorrow et al. 1983; Riley et al. 2016; Nandanwar et al. 2016).

Alkaline traps may also be cooled to improve iodine recovery (Ambade et al. 2015; Joshi et al. 2012). Neutralization reactions of hydroxide with acids such as dissolved NO_x can generate significant heat depending on the solution volume and amount of acidic species; cooling the trap can alleviate this problem.

If desired, redox reagents can be added to the alkaline solution to alter the iodine species. Addition of reducing agents such as SO_3^{2-} or $S_2O_3^{2-}$ will convert the iodine species to I^-, which could improve the alkaline trap performance by improving conversion of I_2 to I^- more than the use of hydroxide alone. Conversion of iodine to I^- also allows for further processing using methods like ion exchange chromatography for recovery of iodine or regeneration of the hydroxide trap. Addition of oxidizing agents like KNO_2 or H_2O_2 will convert the iodine species to I_2, which allows for further processing using methods like distillation or solvent extraction with a non-polar solvent such as CCl_4. Oxidizing agents will also remove any reducing agents like SO_3^{2-} from the solution (Trevorrow et al.1983; Riley et al. 2016).

The next three sections provide examples of the use of alkaline traps, redox reagents, etc. for collecting and purifying iodine from different types of samples to demonstrate how these systems could be implemented.

2.2.2.1 Collection of ^{131}I from Irradiated TeO_2 Using Distillation

Ambade et al. (2015) designed a distillation method for collecting ^{131}I from irradiated TeO_2 for radiopharmaceutical use. Figure 2-1 shows a diagram of the distillation apparatus; the apparatus was used in a shielded cell capable of handling 100 Ci ^{131}I per batch. A carrier gas stream of air at a flow rate of 20–30 mL/min was used to bubble the I vapor from the dissolution vessel through the two alkaline traps followed by a Ag-impregnated charcoal trap to remove any iodine vapor not captured in the alkaline traps. Each alkaline trap contained 8 mL 0.1 M NaOH with 0.2 mg/mL Na_2SO_3 and was cooled to maximize iodine recovery. Experimental results showed 70% of the iodine was present in the first trap and 30% in the second trap (Ambade 2015).

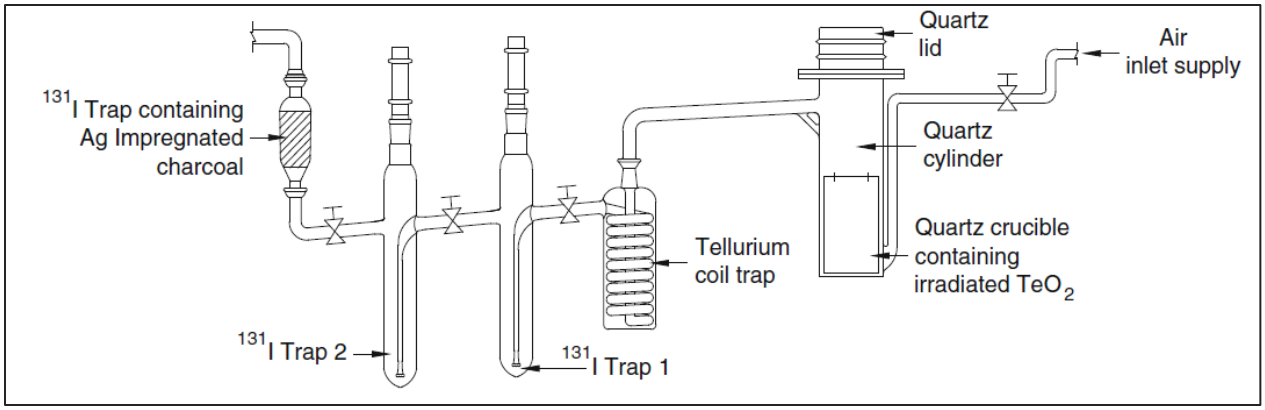

Figure 2-1. Distillation apparatus for collection of ^{131}I following irradiation of TeO_2 (Ambade 2015)

In the distillation apparatus set up by Ambade et al. (2015) iodine reacts with OH^- to form I^- and IO_3^-. Iodate is reduced to I^- by adding thiosulphate ($S_2O_3^{2-}$) or sulfite (SO_3^{2-}). In addition to NaOH, the alkaline trap can be composed of other alkaline species such as KOH, $Ca(OH)_2$, NH_4OH, or Na_2CO_3 (Ambade et al. 2015).

$$3\,I_{2(g)} + 6\,NaOH_{(aq)} \rightarrow 5\,NaI_{(aq)} + NaIO_{3(aq)} + 3\,H_2O \qquad \text{Equation 2-9}$$

$$NaIO_{3(aq)} + 3\,Na_2SO_{3(aq)} \rightarrow NaI_{(aq)} + 3\,Na_2SO_{4(aq)} \qquad \text{Equation 2-10}$$

$$NaIO_{3(aq)} + 3\,Na_2S_2O_{3(aq)} \rightarrow NaI_{(aq)} + 3\,Na_2SO_{4(aq)} + 3\,S_{(s)} \qquad \text{Equation 2-11}$$

2.2.2.2 Collection of ^{125}I from Irradiated Xe Using Distillation

Joshi et al. (2012) designed a method to recover ^{125}I from irradiated Xe using distillation; the distillation apparatus is shown in Figure 2-2. Following irradiation of a Xe target, the ^{125}I was dissolved in 70 mL 0.03 M Na_2SO_3 to generate an I^- solution. Iodide was oxidized to IO_3^- by adding H_2SO_4 until the solution was 18 M followed by 5 mL 0.1 M $KMnO_4$; the solution was refluxed for 1 hour. Iodate was converted to I_2 by addition of 5 mL 0.2 M oxalic acid. The I_2 solution was distilled with the I_2 vapor bubbled through a capillary tube containing 0.5 mL 0.1 M NaOH with 0.2 mg/mL Na_2SO_3 to generate a I^- solution; the alkaline trap was cooled to maximize iodine recovery. Joshi et al. found that the distillation temperature was extremely important because it affects how much I_2 is evolved vs how much remains solubilized; the maximum temperature tested was 120°C, because the quartz apparatus could not withstand the pressure generated above that temperature. Under these conditions, optimum yield was obtained after 250 minutes (Joshi 2012).

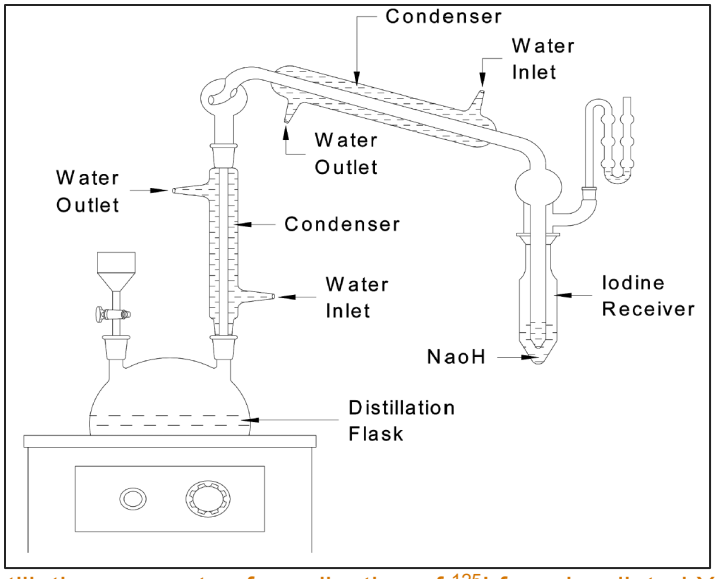

Figure 2-2. Distillation apparatus for collection of ^{125}I from irradiated Xe (Joshi 2012)

2.2.2.3 Collection and Purification of Iodine from Conifer Samples

Quintana et al. (2000) designed a method to recover iodine from conifer samples using distillation followed by solvent extraction; the distillation apparatus is shown in Figure 2-3. Following dissolution using alkaline fusion with KOH and K_2SO_3, the solution was acidified by adding HNO_3 and 2 mg KI carrier was added. The solution was distilled for 2 hours and 2–3 mL 0.5 M KNO_2 was added every 30 minutes. KNO_2 is an oxidizing agent that will convert I^- to I_2, as shown in Equation 2-, and eliminate any remaining K_2SO_3. I_2 was collected in two sequential alkaline traps containing respective solutions of 80 mL and 60 mL of 0.75 M KOH with 0.5 g K_2SO_3. Iodine recovery was 95–98% following this distillation; the distillation efficiency depends on the solution acidity and the gas flow rate (Quintana and Thyssen 2000).

$$2\,KNO_{2(aq)} + 2\,KI_{(aq)} + 4\,HNO_{3(aq)} \rightarrow 2\,NO_{(g)} + I_{2(g)} + 4\,KNO_{3(aq)} + 2\,H_2O \qquad \text{Equation 2-12}$$

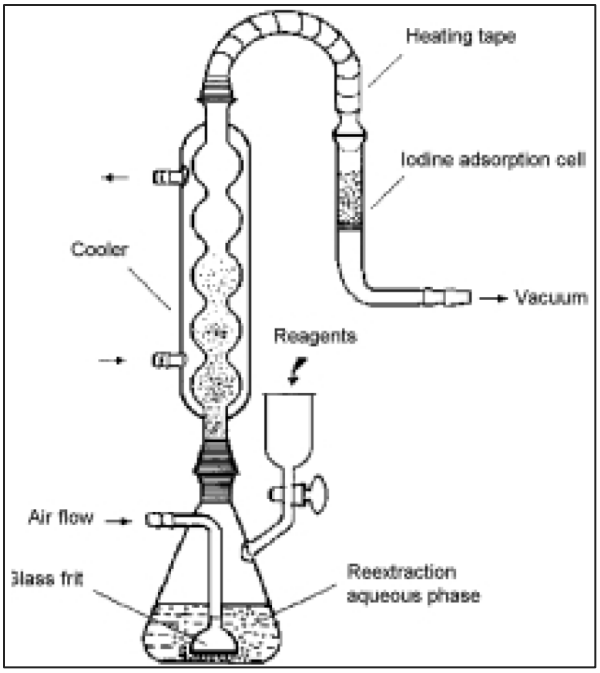

Figure 2-3. Distillation apparatus for collection of iodine from conifer samples (Quintana 2000)

Quintana et al. (2000) recovered iodine from the alkaline traps using solvent extraction with CCl_4. The alkaline trap solutions were acidified by adding concentrated HNO_3 followed by 2–3 mL 0.5 M KNO_2. I_2 was extracted into CCl_4 using 2–3 extractions with 80 mL CCl_4. Iodine was back-extracted twice using 100 mL H_2O with 200 mL K_2SO_3. Quintana et al. (2000) reported a 5–8% iodine loss during the solvent extraction but noted additional extractions could reduce this loss.

Quintana et al. (2000) followed the solvent extraction with a second distillation. The extraction solution was treated with 1 g $(NH_4)_2MoO_4$ followed by 30 mL concentrated H_2SO_4. The sample was then distilled within 2 hours with 2–3 mL H_2O_2/100 mL added every 15 minutes. The reaction of KI, H_2SO_4, and H_2O_2 to produce I_2 is catalyzed by molybdate, as shown in Equation 2-13. The degradation of H_2O_2 to O_2 (Equation 2-15) helps flush I_2 through the system. I_2 was collected using 0.5 g KI-impregnated activated charcoal. The total process resulted in 90–95% iodine recovery.

$$H_2O_{2(aq)} + 2\,KI_{(aq)} + H_2SO_{4(aq)} \rightarrow I_{2(g)} + K_2SO_{4(aq)} + 2\,H_2O \qquad \text{Equation 2-13}$$

$$2\,KI_{(aq)} + H_2SO_{4(aq)} \rightarrow I_{2(g)} + K_2SO_{3(aq)} + 2\,H_2O \qquad \text{Equation 2-14}$$

$$2\,H_2O_{2(aq)} \rightarrow O_{2(g)} + 2\,H_2O \qquad \text{Equation 2-15}$$

Quintana et al. (2000) showed it was possible to recover iodine in high yield and purity through a series of chemical steps (listed below) using the reducing agent K_2SO_3, the oxidizing agents KNO_2 and H_2O_2, and a $(NH_4)_2MoO_4$ catalyst, as well as purification using distillation and solvent extraction with final collection on a charcoal trap:

- Dissolve conifer samples in KOH / K_2SO_3 to generate an alkaline solution of I^-

- Acidify the alkaline I^- solution with HNO_3 then oxidize it to I_2 using KNO_2.
- Distill I_2 and collect I^- in 2 KOH/K_2SO_3 traps.
- Again, acidify the alkaline I^- solution with HNO_3, then oxidize it to I_2 using KNO_2.
- Extract I_2 into CCl_4, then back-extract I^- into H_2O/ K_2SO_3.
- Add $(NH_4)_2MoO_4$ followed by H_2SO_4, then add H_2O_2 during a second distillation to catalyze the reaction of I^- to I_2.
- Collect I_2 on a KI-impregnated activated charcoal trap.

2.2.3 Sorbent Materials

Adsorption processes for capturing iodine from a gas stream are based on physical and/or chemical sorption. Physical sorption does not produce a bond between the iodine and the sorbent material and is easily reversed to recover the iodine and/or regenerate the sorbent. Chemical sorption leads to the formation of AgI, which is far more difficult to reverse, making it a good option if the iodine and sorbent will be disposed rather than recovered (Trevorrow et al. 1983). It should be stated that generally inorganic materials are more resistant to radiolytic effects than their organic counterparts.

The Ag sorbents, such as those listed below, are often used in used fuel reprocessing in addition to or instead of alkaline scrubbing, because they are less complicated and less expensive to operate (Trevorrow et al. 1983):

- silver-exchanged zeolite
- silver-exchanged faujasite (AgX)
- silver-exchanged mordenite (AgZ)
- silver-nitrate impregnated amorphous silicic acid (AC-6120)

2.2.3.1 Activated Carbon

Activated carbon (AC) is a carbonaceous material that has a large specific surface area (300–4000 m^2/g), an easily tuned structure and porosity with pore sizes ranging from 4.5–60 Å, good adsorption capacities, and low production costs (Huve et al. 2018). AC is an effective sorbent for iodine capture because of its high surface area and pore size, and it works by using physical sorption processes. I_2 will sorb to AC at elevated temperatures, but, as the temperature increases I_2 will desorb because it is not chemically bound to the sorbent. The sorption capacity for AC can be optimized by controlling for a variety of factors including the following (Nandanwar et al. 2016; Huve et al. 2018):

- selection of raw materials used in the AC synthesis (coal, bamboo, coconut, walnut shells)
- method of preparation and activation – this will affect the surface area and pore size
- impregnation with Ag or compounds such as triethylenediamine (also known as DABCO, 1,4-diazabicyclo[2.2.2]octane)
- altering the functional or phenolic group.

AC has a low autoignition temperature and contact with compounds like NO_x reduces the iodine sorption capacity and can lead to the formation of explosive compounds; for these reasons AC is not used in used fuel reprocessing plants (Nandanwar et al. 2016; Huve et al. 2018). Placing

an AC trap after an alkaline trap ensures that no NO_x enters the AC trap and helps ensure that any iodine that does not react with the hydroxide is removed from the gas stream.

AC can be impregnated with KI or organic compounds like TEDA (Nandanwar et al. 2016; Huve et al. 2018; NUCON 2011). CH_3I sorbs to AC impregnated with KI through isotope exchange and to AC impregnated with TEDA through chemisorption; both reactions are more efficient at elevated temperatures. Optimizing the sorption of CH_3I includes factors such as flow rate, bed volume, and particle size in addition to the temperature; a higher gas flow rate decreases the residence time and CH_3I sorption while decreasing the particle size increases CH_3I sorption. AC is hygroscopic and absorbed water competes with iodine sorption; above 95% relative humidity the absorption of CH_3I is dramatically reduced. AC is more resistant to humidity when impregnated with TEDA (NUCON 2011). Experimental results have demonstrated that 5% TEDA loaded on AC/120 sorbent removed 98% of CH_3I from humid air at 303 K and 1 atm. Organic iodides can be difficult to capture, making TEDA-impregnated AC a good choice if the gas stream is expected to contain a significant quantity of organic iodides (Nandanwar et al. 2016).

As with the zeolite materials discussed in the following sections, AC can be impregnated with Ag to make use of the chemical sorption process generating AgI. In this case, I_2 will sorb to the material using both physical and chemical sorption processes and can only be partially regenerated (Nandanwar et al. 2016).

In addition to the sorption of gaseous I_2, AC (with or without Ag) can sorb iodide from solutions. For AC impregnated with Ag, iodide sorption is initially controlled by precipitation of AgI. Once the Ag is consumed, iodide may be adsorbed to the AC, which increases as pH decreases; lower pH corresponds to a more positively charged surface and less competition from hydroxide ions (Hoskins et al. 2002). Alternatively, iodide is converted to I_2 as the pH decreases (to around pH 5) and I_2 sorbs to the AC (Watson et al. 2016).

2.2.3.2 Silver-exchanged Zeolites

Zeolites are naturally alumina- and silica-containing compounds that can physically sorb iodine. They can also be converted to a silver-exchanged form, which results in chemical sorption in addition to physical sorption; physically sorbed iodine is easily displaced through heating while chemically sorbed iodine is not (Trevorrow et al. 1983). Silver-exchanged or -impregnated sorbents demonstrate high iodine sorption at high temperatures (i.e., 423K) making them a better option for higher temperature processes than AC (Nandanwar et al. 2016).

Silver-exchanged faujasite (AgX) is a Linde-type 13X molecular sieve that has high porosity. This material is commercially available in the Na form, which can be easily converted to the Ag form. At 150°C, the typical loading reported is 349 I_2/g AgX, where 214 mg/g is sorbed chemically and 135 mg/g is sorbed physically (Trevorrow et al. 1983).

Silver-exchanged mordenite (AgZ) has a higher silica-to-alumina ratio than silver-exchanged faujasite, which results in increased hardness, resistance to acid decomposition, but only around 1/3 the ion exchange capacity of AgX. Chemical sorption can be increased compared to physical sorption by pretreating AgX with H_2 gas at 500°C for around 16 hours prior to use, which converts Ag^+ to the metal (Trevorrow et al. 1983).

2.2.3.3 Silver-nitrate-impregnated Amorphous Silicic Acid

Amorphous silicic acid impregnated with $AgNO_3$, such as AC-6120, sorbs I_2 and CH_3I by chemically reacting to form AgI and $AgIO_3$; elevated temperature (i.e., 150ºC) ensures the organic iodide reacts with the sorbent. These sorbents provide a high-percentage utilization of the Ag making them quite efficient. The addition of 1–10% NO_2 has been shown to improve the performance of these sorbents by preventing reduction of Ag to the metal state. The sorbents can be adversely affected by high humidity or the presence of organic contaminants (Nandanwar et al. 2016; Haefner and Tranter 2007).

Amorphous silicic acid impregnated with $AgNO_3$ is 3–10 times less expensive than Ag zeolites, is resistant to NO_X, and unlike AC will not form flammable or explosive compounds. However, these sorbents cannot be regenerated (Nandanwar et al. 2016; Haefner and Tranter 2007).

2.2.3.4 Comparison of Ac and Ag-exchanged Sorbents

A comparison of AC and Ag-exchanged sorbents for use in iodide capture is shown in Table 2-7.

Table 2-7. Comparison of AC and Ag-exchanged sorbents for iodine removal (Kang and Kleinberg 2020; Huve et al. 2018)

	Activated Carbon (AC)	Silver-exchanged Faujasite (AgX)	Silver-exchanged Mordenite (AgZ)
Iodine sorption capacity	• AC > AgX > AgZ		
Iodine sorption	• Extremely high iodine sorption, can sorb both I_2 and CH_3I • Sorption is affected by humidity (>40%) • Iodine-loaded AC holding capacity decreases with time	• A significant portion of the captured iodine may become re-volatilized as time passes (physisorbed iodine) • A significant portion of the iodine is chemisorbed and will not re-volatilize	
Temperature	• AC can ignite at a relatively low temperature (~200°C) • Iodine sorption decreases with increasing temperature (>80°C)	• Stable at higher temperatures than AC	• Stable at higher temperatures than AC or AgX
Chemical resistance	• The ignition temperature can be lowered following exposure to chemicals like organics or NO_x; explosive materials can be formed	• Not acid resistant and must be coupled with an alkaline scrubbing system	• Higher chemical and acid resistance than AgX
Additional information	• Easily produced commercially • Sensitive to aging • Can be impregnated with KI or TEDA to increase the capture of radioiodine	• High cost • Highly regulated material by the U.S. Environmental Protection Agency • Using metals other than Ag usually leads to lower performance; Bi-doped mesoporous silica shows high adsorption of iodine and thermal stability of the captured iodine	

2.2.4 Capture of HIO

HIO can be difficult to remove from the gaseous stream and little to no HIO sorbs to AFAS-I filters. For solid sorption methods, the highest sorption of HIO was shown to be OU-A carbon impregnated with $AgNO_3$ followed by OU-A carbon impregnated with triethylene diamine and hyposulfite. Only small amounts of HIO have been shown to be absorbed by water or water containing active substances including sulfuric acid, potassium hydroxide, hyposulfite, hydrogen peroxide, or triethylene diamine. Organic solvents are better at absorbing HIO than aqueous solutions, including carbon tetrachloride, ethanol, and polymethylsiloxanes such as PMS-10 (Borisov 2004).

2.3 Chemical Separations

2.3.1 Column Chromatography

A variety of chromatographic separations can be used to separate various iodine species from isotopes of interest like ^{99}Mo, FP impurities, alkaline traps, etc. One method described for use in the processing of radioactive waste solutions is the use of a mixed resin bed containing CL resin loaded with Ag and XAD-4 resin. CL resin loaded with Ag^+ sorbs I^- and IO_3^-, while XAD-4 is a non-polar polyaromatic adsorbent designed for small hydrophobic compounds and chlorinated organic compounds and sorbs I_2 (Decamp and Happel 2013).

CL resin is available from Eichrom Technologies (in the United States); this resin uses an extractant selective for gold, silver, and platinum group metals such as Pd^{2+}. When loaded with Ag+, the resin has a higher capacity for Cl^-, I^-, and IO_3^-. For processing I^- and IO_3^-, the resin can be loaded in mildly acidic or neutral conditions and rinsing the column with dilute alkaline solution like 1% NaOH prior to elution increases the iodide yield. Iodide can then be eluted in a variety of eluents, including Na_2S, NH_3, NH_4OH, alkali cyanides, etc., that solubilize AgI and $AgIO_3$. CL resin loaded with Ag^+ has a high affinity for I^- and IO_3^- with a loading capacity of 25 mg I^- per gram CL resin loaded with 20 mg Ag^+ (Decamp and Happel 2013).

Decamp and Happel (2013) reported the use of this mixed bed resin for use at IRE, a ^{99}Mo producer located in Belgium. After dissolving the U-Al alloy in an alkaline solution, the solution was acidified to 1 M HNO_3 and ^{99}Mo was removed using an alumina column. The mixed CL resin loaded with Ag^+ and XAD-4 resin was then used to remove iodine species from 1 M HNO_3. The iodine retention was dependent on the CL resin grade, flow rate, and total volume of solution. Mo-99 should not sorb to the CL resin with or without Ag^+ or the XAD-4 resin so that a separation involving primarily ^{99}Mo and iodine species would not require an alumina column.

2.3.2 Solvent Extraction

It is possible to separate I_2 from other iodine species, FP, etc. or recover I_2 from an alkaline trap using solvent extraction. I_2 is soluble in a variety of non-polar organic solvents such as CCl_4, toluene, etc. Oxidizing agents like KNO_2 or H_2O_2 can be used to convert I^- and IO_3^- to I_2 and will destroy any reducing agents present in the system like SO_3^{2-} added to ensure iodine was present as I^-. I_2 can be back-extracted as I^- using aqueous solutions of NaOH, SO_2, or $NaHSO_3$. (Kahn and Kleinberg 1977).

3.0 Tellurium Chemistry

A wide array of fission products (FP) is produced when irradiating uranium including radioactive tellurium isotopes which decay into radioiodine isotopes. Some of the Te isotopes have long enough half-lives that they are present during processing for medical isotopes, such as ^{99}Mo, creating a source of radioiodine in parts of the process where the chemistry differs from iodine chemistry. In addition to accounting for the iodine present at the end of irradiation, complete abatement of radioiodine emissions depends on understanding the chemistry of the parent Te isotopes to design a system which can address these various radioiodine sources. This section provides an overview of Te chemistry.

3.1 Tellurium Speciation

Tellurium speciation is complex with the potential for multiple oxidation states existing simultaneously as well as multiple chemical species for each oxidation state co-existing; the most stable oxidation states for Te are -2, +4, and +6. The oxidation states and speciation are dependent on a range of variables including Te concentration, temperature, pH, matrix composition, and the presence of reduction-oxidation (redox) active species. The complex chemical behavior of Te contributes to the common problem of chemical fractionation during processing. (Leddicotte 1961)

3.1.1 Tellurium Concentration

Tellurium speciation is dependent on the tellurium concentration and the use of carrier can improve the chemical separation efficiency. Carrier can be added at various steps during sample processing (before dissolution, after dissolution, etc.) but it is critical that the carrier be in the same chemical form as the Te in the dissolver solution. In a HCl or HNO_3 system, a commercially available ICP standard may be used as a well characterized Te carrier source. It is also possible to prepare fresh Te carrier solutions from a starting material of choice and/or use a chemical redox reaction to convert all Te atoms to the same chemical form. (Leddicotte 1961)

3.1.2 Acidic and Alkaline Matrices

Tellurium speciation is dependent on the solution pH, the matrix composition, and the matrix concentration. As shown in **Error! Reference source not found.**, in alkaline and very dilute acidic solutions Te is present as the cationic TeO^{2+}. As the solution acidity increases, Te will start to form tellurites in the form of TeO_3^{2-}. As the solution acidity continues to increase in an oxidizing matrix like HNO_3, Te will start to form the oxidized tellurate species TeO_4^{2-}. In a matrix with coordinating anions like Cl^-, Te will form complex species as the anion concentration increases. (Leddicote 1961)

Table 3-1. Tellurium speciation under different acidic and alkaline conditions (Ledicote 1961)

Te Oxidation State	Matrix	Te Species
Te(IV)	Alkaline	TeO^{2+}
Te(IV)	pH > 3	TeO_3^{2-}
Te(IV)	Dilute HNO_3	TeO^{2+}
Te(IV)	6 M HNO_3	TeO^{2+}, TeO_3^{2-}

Te(VI)	6 M HNO_3	TeO_4^{2-}
Te(IV)	0.5 – 2 M HCl	TeO^{2+}
Te(IV)	4 – 6 M HCl	$TeOCl_4^{2-}$
Te(IV)	9 – 12 M HCl	$TeCl_6^{2-}$

3.1.3 Volatility

Tellurium forms volatile species under a variety of conditions such as the semi-volatile TeO_3. Volatilization from hot acidic solutions can be prevented by keeping the temperature < 100°C. The presence of alkali salts do not prevent volatilization from boiling solutions. If volatilization of Te is desired, Te(IV) can be volatilized by passing Cl_2 gas through a hot HCl solution and $TeOCl_2$ is volatile at > 100°C in 6 M HCl. (Leddicotte 1961)

3.2 Chemical Separations for Tellurium

3.2.1 Precipitation

Tellurium can be separated from a complex solution by precipitation of elemental (i.e., metallic) Te, TeO_2, or co-precipitation. The precipitation of elemental Te or TeO_2 does require sufficient Te mass to ensure there is sufficient precipitate to enable separation from the solution through filtration or centrifugation; Te carrier can be added to the solution if needed. The need for Te carrier can be avoided using co-precipitation where Te will precipitate along with another element or will sorb to the precipitate that forms. Examples of precipitates which can be used for separation of Te include CuS, RuS_2, $Fe(OH)_3$, and Se metal. (Leddicotte 1961)

With an appropriate reductant, Te can be reduced to elemental Te. The primary limitations to this method are 1) the reduction does not work under oxidizing conditions such as HNO_3 solutions and 2) in the absence of a reducing agent Te will oxidize and dissolve (Leddicotte 1961). A variety of reductants can be used including (Leddicotte 1961):

- Tellurium salts in strong acid solutions:
  - Sulfur dioxide
  - Hydrazine hydrochloride
  - Hydrazine
  - Hypophosphite
  - Potassium iodide
  - Vandyl sulfate
  - Stannous chloride

- Tellurides in acidic solutions:
  - Titanous chloride
  - Aluminum
  - Phosphorus
  - Hypophosphorus acids

In addition to elemental Te, Te may be precipitated as TeO_2 with pyridine or hexamine and lead tellurate may be precipitated from a solution of lead nitrate and sodium tellurate. (Leddicotte 1961)

3.2.2 Column Chromatography using Ion-Exchange

Tellurium forms a variety of chemical species and complexes depending on the matrix composition, matrix pH, etc.; Te species expected in HNO_3, HCl, and alkaline conditions are given in **Error! Reference source not found.Error! Reference source not found.Error! Reference source not found.**. Ion-exchange chromatography using anion-exchange or cation-exchange resins can be an efficient method for separating a variety of analytes.

3.2.2.1 Example 1: Precipitation with ion-exchange chromatography

The use of reductants to convert Te to the elemental form can be combined with ion-exchange chromatography. If loaded onto an anion-exchange column in the Sn(II) form in a non-oxidizing matrix such as HCl, Te will convert to the elemental form and remain adhered to the column. Alternately, once the sample has been loaded onto the column, adding a rinse with $SnCl_2$ or SO_2 in 6 M HCl will convert Te to the elemental form on the column. The column can be rinsed with a non-oxidizing eluent such as 1 M HCl to elute co-adsorbed analytes. The elemental Te can be dissolved by rinsing with an oxidant such as 30% H_2O_2 or any concentration of HNO_3. Tellurium can be eluted with an eluent where it is primarily in the cationic state such as 1 M HCl or 1 M NaCl. (Korkisch 1989)

3.2.2.2 Example 2: Separation of iodine and tellurium with anion-exchange

Hassan et al. (2014) reported the separation of I and Te following irradiation of Sb_2O_3 to produce ^{124}I. The target was dissolved in 7 M HCl and the resulting solution was loaded onto the weak base anion-exchange resin Amberlyst A21. Antimony was eluted with 7 M HCl, I^- was eluted with tetrabutyl ammonium bromide (TBAB) in ethyl acetate with a few drops sodium dithionate, and Te was eluted with 2 M HCl. The chemical yield for iodine was 90 ± 5% with a decontamination of ~$1x10^4$ for Te.

3.2.3 Distillation

Distillation can be used to separate Te from a wide variety of elements including iodine. An example of using distillation in the separation of $^{131}I_2$ from an irradiated TeO_2 target as described by Ambade et al. (2015) is given below. Compared to distillation, the separation of Te from a mixture of elements can be more easily accomplished using techniques such as column chromatography and precipitation. However, the conditions under which Te can be distilled demonstrate the potential conditions where Te can be volatilized during chemical processing.

Ambade et. al. (2015) designed a distillation method for collecting ^{131}I from irradiated TeO_2 for radiopharmaceutical use. Figure 3-1 shows a diagram of the distillation apparatus; the apparatus was used in a shielded cell capable of handling 100 Ci ^{131}I per batch. A carrier gas stream of air at a flow rate of 20-30 mL/min was used to bubble the I_2 vapor from the dissolution vessel through the two alkaline traps followed by a Ag-impregnated charcoal trap to remove any I_2 vapor not captured in the alkaline traps. Each alkaline trap contained 8 mL 0.1 M NaOH with 0.2 mg/mL Na_2SO_3 and were cooled to maximize iodine recovery. Experimental results showed 70% of the iodine was present in the first trap and 30% in the second trap. (Ambade et al. 2015)

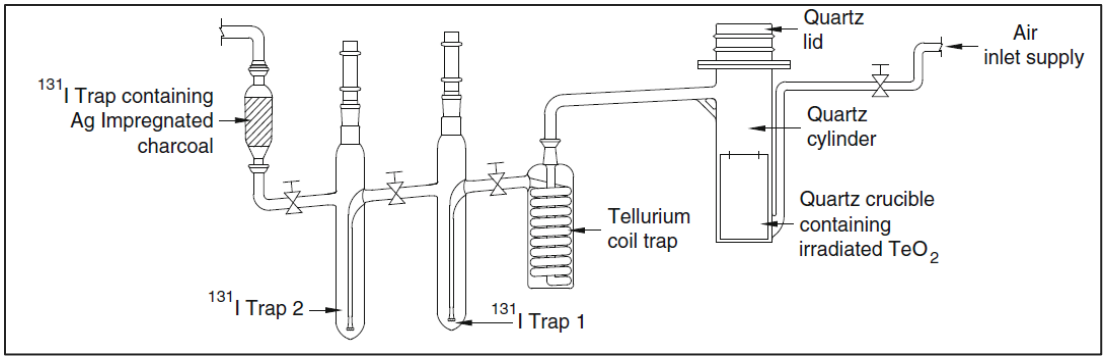

Figure 3-1. Distillation apparatus for collection of ^{131}I following irradiation of TeO_2 (Ambade et al. 2015)

In the distillation apparatus setup by Ambade et. al. (2015), iodine reacts with OH^- to form I^- and IO_3^-. Iodate is reduced to I^- by adding thiosulphate ($S_2O_3^{2-}$) or sulfite (SO_3^{2-}). In addition to NaOH, the alkaline trap can be composed of other alkaline species such as KOH, $Ca(OH)_2$, NH_4OH, or Na_2CO_3.

$$3\,I_{2(g)} + 6\,NaOH_{(aq)} \rightarrow 5\,NaI_{(aq)} + NaIO_{3(aq)} + 3\,H_2O \qquad \text{Equation 3-1}$$

$$NaIO_{3(aq)} + 3\,Na_2SO_{3(aq)} \rightarrow NaI_{(aq)} + 3\,Na_2SO_{4(aq)} \qquad \text{Equation 3-2}$$

$$NaIO_{3(aq)} + 3\,Na_2S_2O_{3(aq)} \rightarrow NaI_{(aq)} + 3\,Na_2SO_{4(aq)} + 3\,S_{(s)} \qquad \text{Equation 3-3}$$

3.2.4 Solvent Extraction

While I_2 is soluble in a variety of non-polar organic solvents (Kahn and Kleinberg 1977), the use of solvent extraction to separate Te is typically accomplished using ion association or chelation making solvent extraction a suitable separation method for I_2 and Te (Leddicotte 1961). With the appropriate counter ion or chelate, Te can be extracted into a variety of organic solvents making it possible to separate Te from a variety of elements. A variety of conditions for Te separation using solvent extraction are shown in Table 3-2. The radiation stability of the solvent, chelate, etc. is a variable to consider when developing a solvent extraction process; the next section discusses radiolysis in a UREX or UREX-like system.

Table 3-2. Some examples of solvent extraction for Te (Leddicotte 1961)

Method	Te Oxidation State	Matrix or Chelate	Organic Solvent	Te Yield
Ion Association	Te(IV)	6 M HCl	Ethyl ether	34%
Ion Association	Te(IV)	7 M HI	Ethyl ether	5.5%
Ion Association	Te(IV)	20 M HF	Ethyl ether	23%
Ion Association	Te(IV)	1 M HNO_3	0.06 – 0.6 M DBPA*	<5%
Ion Association	Te(IV)	Mineral acid / HF (i.e., 6 M HCl – 0.4 M HF)	Diisopropyl ketone	
Ion Association	Te(VI)	Mineral acid / HF (i.e., 6 M H_2SO_4 – 0.4 M HF)	Diisopropyl ketone	
Chelation	Te(IV)	Diethyldithiocarbamate	Chloroform, Benzene, Carbon tetrachloride	

Chelation	Te(IV)	Thiosalicylideneethylenediiamine	Chloroform	
Chelation		Te xanathate / Thiourea	Ether	
*DBPA: di-n-butyl phosphoric acid				

3.2.4.1 Iodine and Tellurium behavior in UREX or UREX-like Extraction Systems

The general extraction process for tributylphosphate (TBP) based extraction using Te(IV) as the example for the extracted metal from an HCl matrix is shown in Equation 3-4 (Bandyopadhyay et al. 1996). A similar extraction mechanism is expected from a HNO_3 system.

$$Te(IV)_{(aq)} + 3\,TBP_{(org)} + 4\,Cl^-_{(aq)} \rightarrow 3\,TeCl_4 * TBP_{3(org)} \qquad \text{Equation 3-4}$$

The extraction efficacy of Te from HNO_3 matrix is relatively low, reaching a peak of ~25% at ~6 M HNO_3 using 30% TBP in cyclohexane (El-sweify and Metwally 2007). El-sweify and Metwally showed that the organic solvent has a significant effect on the extraction of Te(IV) where nitrobenzene > $CHCl_3$ > CCl_4 > p-xylene > benzene > toluene > cyclohexane. Direct parallels can be drawn between the solvent effects seen in the El-sweify and Metwally experiments and more commonly used solvents such as kerosene or dodecane, whose solvent behavior should be more similar to cyclohexane than an aromatic solvent such as benzene or toluene. At 3 M HNO_3, El-sweify and Metwally found ~15% extraction of Te(IV) using 30% TBP in cyclohexane. Though the extraction of Te is low, Te is a high yield fission product that will be extracted to an extent into the extraction solvent and therefore be a source of radioiodine daughters.

Iodine (I_2) is readily extracted into organic solvents, as mentioned above. Due to the extraction of I_2 by the solvent, one of the primary concerns is the radiolytic degradation of the solvent outside of what would be expected from the UREX or UREX-like extraction system i.e. extraction using TBP from HNO_3. It is this radiolytic decay and subsequent chemistry between iodine and degradation products that is a significant source of the organic iodide complexes. Tributylphosphate (TBP) has widespread usage for the separation of irradiated U and a wealth of knowledge on the radiolysis of TBP has been generated (Choppin et al. 2002; Mincher et al. 2009). The primary decay products of TBP include phosphoric acid, dibutyl hydrogen phosphate (HDBP), and butyl dihydrogen phosphate (H_2BP), shown below in Figure 3-2. In the case of HDBP there are multiple pathways to obtain the same product including radicals stemming from water, extracted nitric acid, from another TBP molecule or fragment, and the diluent, such as dodecane, examples of radical formation on TBP are shown in Table 3-3. (Mincher, et al. 2009; Mincher et al. 2008) The further degradation of the HDBP will occur sequentially until there is phosphoric acid and butene. (Mincher et al. 2009; Pearson and Nilsson 2014) Production of these TBP radiolysis products decreases with the number of cleaved butyl groups (HDBP>H_2BP>Phosphoric acid) (Mincher et al. 2009; Pearson and Nilsson 2014). Unless scrubbed from solution these TBP radiolysis products persist in the extraction solvent, altering the extraction behavior, although there needs to be a significant quantity of these products to cause significant issues.

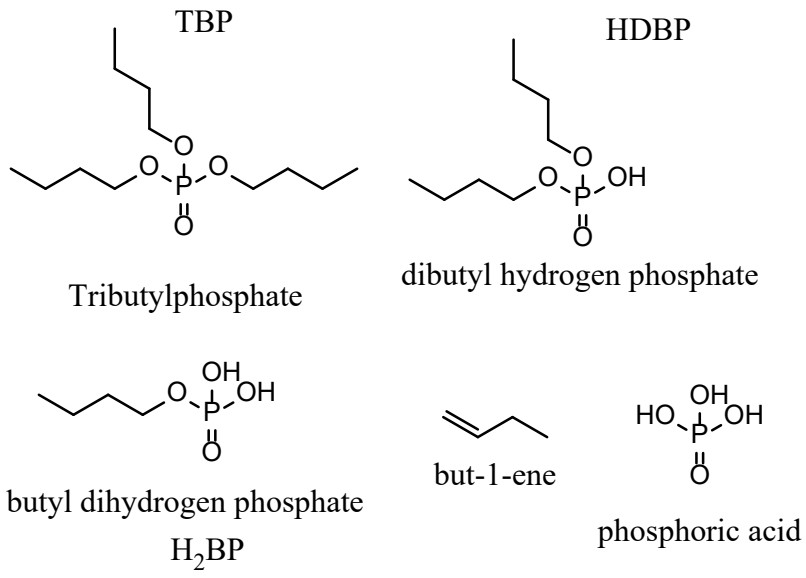

Figure 3-2. Primary Radiolytic Products of TBP under Radiation (Mincher et al. 2009)

Table 3-3. Examples of Radical Formation Involving TBP (Mincher, et al. 2009; Mincher et al. 2008)

$(\bullet C_4H_8O)(C_4H_9O)_2PO \rightarrow (C_4H_9O)_2OPO^- + \bullet C_4H_8$
$\bullet H + TBP \rightarrow (\bullet C_4H_8O)(C_4H_9O)_2PO + H_2$
$\bullet OH + TBP \rightarrow (C_4H_9O)_2(\bullet C_4H_8O)PO + H_2O$

The radiolytic degradation of TBP is impacted by the presence of iodine in solution (Nowak and Nowak 1986). In general, there is a slight retardation in the radiolysis of TBP when I^- is present, though this is also dependent on the HNO_3 concentration. This extraction system is also known to extract I_2, though other reactions are known to occur such as the formation of the I_3^- species in solution (Nowak and Nowak 1986; Sakurai, et al. 1995). Iodine is readily extracted by 30% TBP extraction solvents, where heavily irradiated solutions may produce a third phase (Sakurai, et al. 1995). In solutions containing a significant quantity of iodine, the formation of organic iodides is promoted through interaction between the iodine and the organic degradation products from the extraction solvent (Nowak and Nowak 1986; Sakurai, et al. 1995).

4.0 Materials and Methods

4.1 Materials

Sodium iodide, silver nitrate, Amberlite XAD-4 resin, and all acids (as Optima grade) were purchased from Fisher Scientific. Ammonium molybdate was obtained from Baker. Tellurium was obtained from Inorganic Ventures as a single element standard in either 10% HNO_3 or 30% HCl, the Te in HNO_3 was used in section 4.2 and 4.4 while the Te in HCl was used in section 4.3. Lead (II) nitrate was obtained from Allied Chemical. Tin (II) chloride was obtained from Alfa Aesar. SR and CL resins, 100-150 µm, were obtained from Eichrom Technologies. All chemicals were used as received without further purification.

Samples were analyzed on a Thermofisher iCAP PRO ICP-OES and/or an Agilent 7700 ICP-MS. When analyzed via HPGe, see section 4.2, samples were analyzed via Mirion HPGe systems using Canberra Genie 2000 V3.4.1 and APEX software. HPGe detectors were calibrated using NIST traceable multi-element standards from Eckert and Ziegler.

Deionized (DI) water was prepared at 18.2 mΩ using a Thermo Scientific™ Barnstead™ GenPure™ water purifier.

To prepare tracer solutions, a known mass of sodium iodide and ammonium molybdate were dissolved in a known mass of DI H_2O and a known mass of Te ICP standard was diluted in the acid media of choice (3 M HNO_3 for sections 4.2 and 4.4 and pH 1 H_2SO_4 for section 4.3) and the final mass taken. Immediately before use, the sodium iodide/ammonium molybdate solution was added to the tellurium solution, reweighed to determine final concentrations, and used.

4.2 SR Resin Loaded with Pb

Two different experiments were conducted with SR resin loaded with Pb^{2+}. In both experiments columns were prepared by mixing 3 grams of SR resin and enough $Pb(NO_3)_2$ to load the resin in 3 M HNO_3 overnight. The resin was transferred to 0.8 cm ID Bio-Rad poly-prep columns to a volume of 2 mL. Each column was rinsed with 10 mL of 3 M HNO_3 to remove any unbound Pb.

In the first experiment, samples were prepared with ~100 µg Te, I, and Mo in 2 mL 3 M HNO_3 and loaded onto the columns. Each column was rinsed with three 2 mL aliquots 3 M HNO_3 followed by a rinse of 18 mL DI H_2O. The eluates were collected for analysis by ICP-OES.

In the second experiment, samples were prepared with ~100 µg Te, I, and Mo in 2 mL 3 M HNO_3 along with mixed fission products from an irradiated HEU foil were added, averaging 21 kBq of ^{99}Mo, 14 kBq of ^{132}Te, and 20 kBq of ^{131}I per replicate. The samples were loaded onto the column followed by four rinses with 2 mL aliquots 3 M HNO_3. The eluates were collected for analysis by ICP-OES.

4.3 Precipitation with $SnCl_2$

A solution 5% $SnCl_2$ in H_2SO_4 at pH 1 was prepared. A solution of ~500 ppm Te, ~3,000 ppm I, and ~30 ppm Mo in H_2SO_4 at pH 1 was also prepared. In triplicate, 9 mL 5% $SnCl_2$ solution was contacted with 1 mL of the Te, I, and Mo solution in 50 mL centrifuge tubes. The solution and precipitate were inverted several times and then filtered using Sigma Millipore steri-flip filtration units, contact time was less than 5 minutes. The filtrate was analyzed by ICP-MS.

4.4 CL Resin Loaded with Ag and Amberlite XAD-4 Resin

Columns were prepared by contacting 1.5 grams CL resin, 1.5 grams Amberlite XAD-4 resin, and 0.155 grams $AgNO_3$ in 10 mL of 3 M HNO_3. The resin mixture was loaded into 0.8 cm ID Bio-Rad poly-prep columns, producing enough hydrated resin for four 2 mL columns. A solution was made containing ~100 ppm Te, ~100 ppm I, and ~100 ppm Mo in 3 M HNO_3. All columns were rinsed with 10 mL 3 M HNO_3 to remove any unbound Ag and then loaded with 1 mL of the solution containing Te, I, and Mo (by mass). The columns were rinsed with 1 mL 3 M HNO_3 followed by four 2 mL 3 M HNO_3 rinses. The eluates were collected for analysis by ICP-OES and ICP-MS; the load solution and first 1 mL 3 M HNO_3 rinse were collected as one sample.

5.0 Results

When analyzing via ICP-OES it was determined that it was not possible to reliably yield iodine and ICP-MS was also used for analysis in later experiments. Unfortunately, iodine partitioned into plastic within the ICP-MS during analysis from an acidic solution. Due to this, iodine could not be reliably yielded by ICP-MS. Analysis of solutions in an alkaline matrix would address this problem. It was possible to yield I radiometrically during an experiment using SR resin loaded with Pb^{2+} when an irradiated uranium solution along with the fission products was included in the load solution.

5.1 SR Resin Loaded with Pb^{2+}

Under the appropriate conditions, some species of iodine and Te will react with metals such as Ag and Pb (Leddicotte 1961, Grasser et a. 2021). Decamp and Happel (2013) showed that iodine can be removed from a 1 M HNO_3 solution by passing a solution of irradiated U through a column containing Ag loaded CL resin from Eichrom Technologies. One of the potential downsides to using Ag is the potential for breakthrough especially at higher HNO_3 concentrations. Eichrom Technologies also produces SR resin which strongly retains Pb^{2+} in 0.1-10 M HNO_3 which could potentially remove iodine from a solution with lower breakthrough.

In an initial experiment, a 2 mL SR column was loaded with Pb^{2+} and a solution consisting of ~100 µg Te, I, and Mo in 3 M HNO_3 was allowed to elute through by gravity. After loading the sample, the columns turned an intense yellow due to the formation of PbI_2, see Figure 5-1. The results showed each 2 mL 3 M HNO_3 rinse eluted 45 µg Pb, ~0.1% of the Pb loaded. Approximately 40% of the Pb loaded, 12 mg, eluted in the 18 mL DI H_2O rinse; this is expected since Pb sorbs to SR resin in 0.1-10 M HNO_3. The intense yellow color disappeared with the H_2O rinse indicating it is possible to elute PbI_2 from the column. Results also showed neither Mo nor Te sorbed to the Pb loaded SR resin; greater than 90% Mo and Te eluted in the load and first two 3 M HNO_3 rinses, see Figure 5-2. Molybdenum is not expected to react with Pb^{2+} and should elute in the initial load and rinses. However, Te should react with Pb^{2+} when in the tellurate form indicating most Te is not in the tellurate form; to use Pb loaded SR resin for Te abatement, a redox reagent would be needed to correct the oxidation state.

A more optimal system would include 3 M HNO_3 rinses prior to loading the sample onto the resin to ensure all Pb was thoroughly sorbed to the resin and eliminating a final H_2O rinse unless eluting the material from the column is desired. This experiment was qualitative due to difficulties with yielding iodine by ICP-OES.

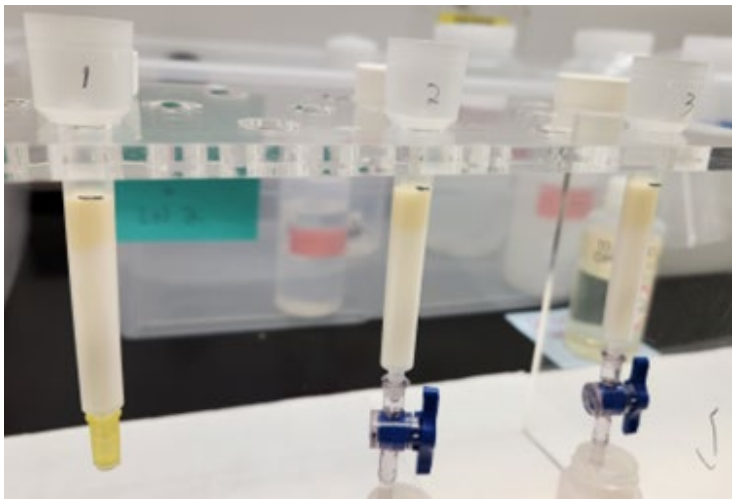

Figure 5-1: Pb loaded SR resin after the second experiment. The yellow color at the top of the column is PbI_2.

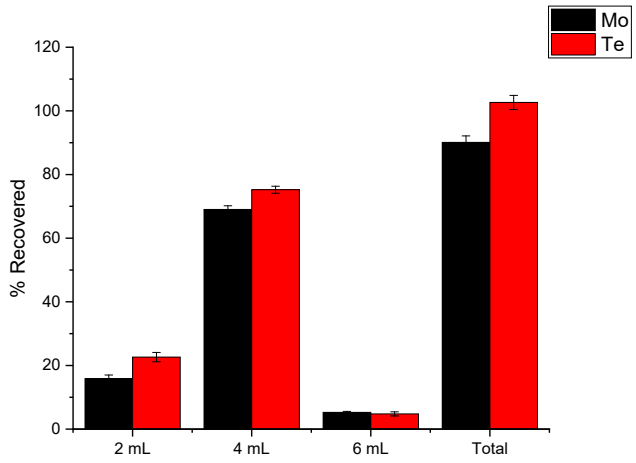

Figure 5-2: Percent Mo and Te recovered in the initial Pb loaded SR resin experiment; sample load contained ~100 µg Te, Mo, and I. No Mo or Te was recovered in the final two fractions (not shown).

A second experiment with Pb load SR resin was performed with an irradiated HEU foil which allowed for yielding iodine through radiometric analysis by HPGe. The results showed that from a sample containing ~100 µg of stable iodide and 20 kBq of ^{131}I separated using a 2 mL Pb loaded SR resin column, ~50% of the ^{131}I eluted the last two HNO_3 rinses as shown in Figure 5-3. Results also showed Mo and Te did not sorb to the Pb loaded SR resin; greater than 90% Mo and Te eluted in the load and first two 3 M HNO_3 rinses while greater than 60% of the U eluted in the first two 3 M HNO_3 rinses.

The Pb2+ loading for this experiment was higher than the first experiment (0.05 vs 0.03 grams Pb per gram resin). The Pb breakthrough was higher in the second experiment with ~70 µg Pb eluting per 2 mL rinse 3 M HNO_3. Pb breakthrough could be avoided through the addition of a second column of SR resin that is not loaded with Pb.

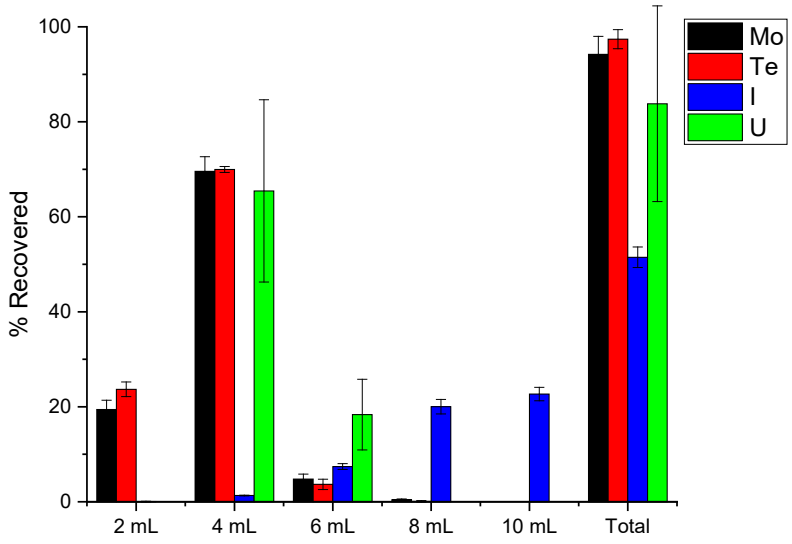

Figure 5-3: Percent Mo, Te, I, and U recovered in the second Pb loaded SR resin experiment.

5.2 Precipitation with $SnCl_2$

A solution of Te, I, and Mo in H_2SO_4 was contacted with a solution of 5% $SnCl_2$ in H_2SO_4; both solutions were at pH 1. Tellurium and iodine should precipitate with Sn^{2+} while Mo should not precipitate; this method will not work with in the presence of an oxidizer such as NO_3^- and must be performed in solutions of either neutral or reducing acids such as HCl and H_2SO_4. The results are shown in Figure 5-4. The amount of Te remaining in solution is < 10%, the amount of Mo remaining in solution is 40-100%, and iodine is not reported as it clung to the plastic tubing of the instrument The large quantity of Sn present is due to the redox reagent being in excess to make sure that the Te was adequately reduced.

The reaction time was less than 5 minutes and agitation were not applied other than turning the tubes over a few times. It may be that the Te removal would be greater with a longer reaction time and greater agitation and that Mo might have co-precipitated or adhered to the precipitate in some of the samples. It may be possible to reduce the removal of Mo from the solution with through rinsing or by dissolving the solid and performing the precipitation a second time. Further

work is likely required to optimize this process, with a more effective analytical method for iodine quantitation.

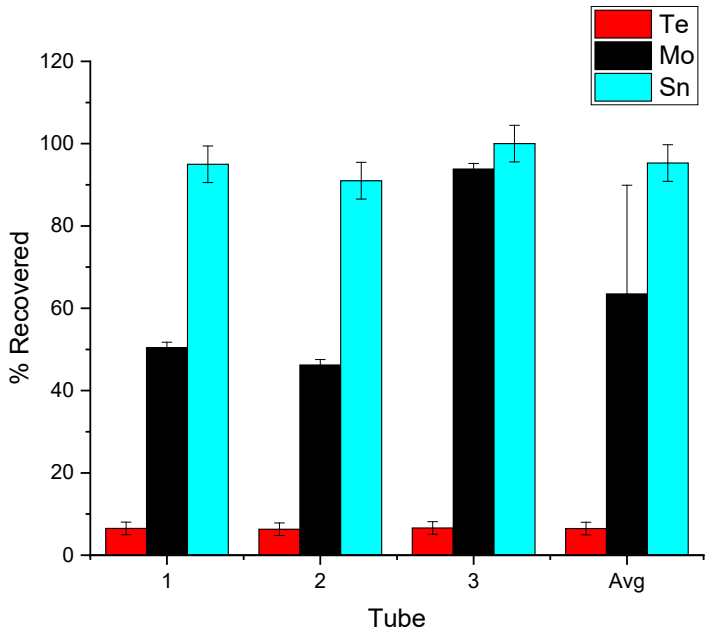

Figure 5-4: Percent Te, Mo, and Sn recovered in the $SnCl_2$ experiment.

5.3 CL Resin Loaded with Ag and Amberlite XAD-4 Resin

In the experiments reported by Decamp and Happel (2013), solutions of irradiated U in 1 M HNO_3 were passed through columns composed of CL resin loaded with Ag and Amberlite XAD-4 resin to sorb iodide and iodate to the CL resin by reacting with Ag while I_2 sorbs to Amberlite XAD-4. In the experiment reported here, solutions of Mo, Te, and I were loaded in 3 M HNO_3; the results are shown in Figure 5-5. Neither Mo nor Te show significant sorption to the resins in 3 M HNO_3, and it was determined that < 0.1% of the Ag loaded eluted during the experiment. Iodine stability is not high in HNO_3; therefore, iodine quantitation was not possible using the methods used for the other elements.

As with the SR resin loaded with Pb^{2+}, some species of Te such as tellurate should react with Ag^+ and stick to the resin as a precipitate. The elution of most of the Te indicates that a redox reagent would be needed to adjust the oxidation state to use CL resin loaded with Ag^+ to abate Te.

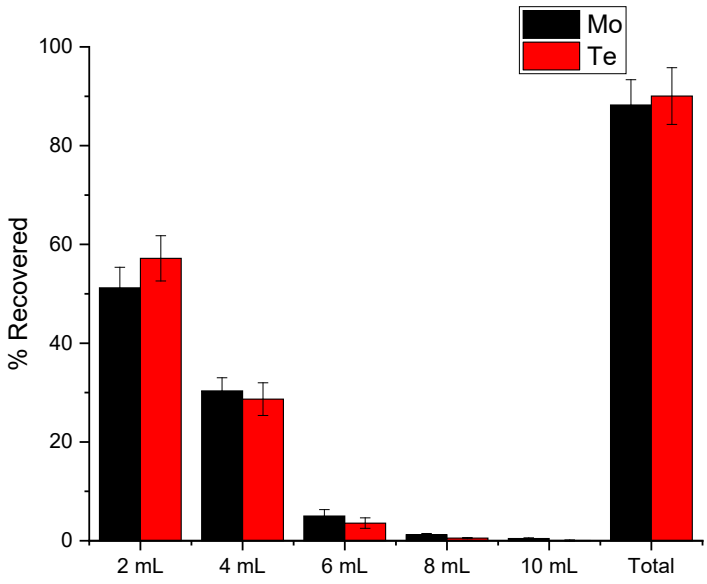

Figure 5-5: Percent recovered of Mo and Te by CL resin loaded with Ag mixed with Amberlite XAD-4 resin in a 1:1 ratio.

6.0 Conclusions

Initial proof-of-concept experiments were performed to test the removal of I and Te from solutions containing Mo for potential abatement during chemical processing to purify ^{99}Mo. The experiments include:

- Column chromatography using SR resin loaded with Pb^{2+} with load solutions in 3 M HNO_3
- Column chromatography using CL resin loaded with Ag^{+} combined with Amberlite XAD-4 with load solutions in 3 M HNO_3
- Precipitation of solutions of I, Te, and Mo with 5% $SnCl_2$ in H_2SO_4

Results from experiments loading solutions of I, Te, and Mo onto SR resin loaded with Pb^{2+} showed that:

- Iodine adheres to the resin as PbI_2 but that there is breakthrough with continuing 3 M HNO_3 rinses,
- Minimal Te adheres to the resin indicating Te is in the wrong oxidation state,
- Minimal Mo adheres to the resin as desired, and
- There is Pb breakthrough with continuing 3 M HNO_3 rinses.

Removal of I and Te from a Mo solution using SR resin loaded with Pb^{2+} could potentially be improved through:

- Altering the concentration of HNO_3 in the load and/or rinses - the optimal concentration of HNO_3 was not tested since this was a proof-of-concept experiment; it appears the PbI_2 is soluble in 3 M HNO_3 and changing the concentration may prevent iodine from eluting.
- Including a redox reagent to alter the Te oxidation state – the introduction of a redox reagent may or may not be practical depending on where in the separation scheme it is included but the results do show the current conditions do not result in Te separation from Mo using this method.
- Altering the Pb loading on the resin – the optimal concentration of Pb on the resin was not tested since this was a proof-of-concept experiment.
- Including a second SR resin column after the Pb loaded column to collect any breakthrough of Pb.

Results from an experiment loading solutions of I, Te, and Mo onto CL resin loaded with Ag^{+} combined with Amberlite XAD-4 showed that:

- Minimal Te adheres to the resin indicating Te is in the wrong oxidation state,

- Minimal Mo adheres to the resin as desired, and
- There is minimal Ag breakthrough with continuing 3 M HNO_3 rinses.
- To obtain results for I, an alternate analysis method such as radiometric detection is needed.

Removal of I and Te from a Mo solution using onto CL resin loaded with Ag^+ combined with Amberlite XAD-4 could potentially be improved through:

- Including a redox reagent to alter the Te oxidation state – the introduction of a redox reagent may or may not be practical depending on where in the separation scheme it is included but the results do show the current conditions do not result in Te separation from Mo using this method.

Results from experiments precipitating solutions of I, Te, and Mo with 5% $SnCl_2$ in H_2SO_4 showed that:

- The amount of Te remaining in solution is < 10%, and
- The amount of Mo remaining in solution is 50-90%.
- To obtain results for I, an alternate analysis method such as radiometric detection is needed.

Precipitating solutions of I, Te, and Mo with 5% $SnCl_2$ in H_2SO_4 could potentially be improved through:

- Te removal might be improved with a longer reaction time (greater than 5 minutes) and greater agitation,
- Removal of Mo from the solution, potentially through co-precipitation or adhering to the precipitate, might be reduced with thorough rinsing or by dissolving the solid and performing the precipitation a second time.

All three proof-of-concept experiments produced results indicating that further optimization could provide methods for I and/or Te abatement. The issue with yielding I would need to be addressed since I is not stable in acidic media and adheres to plastic present in ICP-OES and ICP-MS instruments (such as the sample introduction tubing); analysis in an alkaline media by neutralizing the eluate fractions may be possible. Alternatively, a method such as radiometric detection could be used but requires a radioactive tracer such as ^{131}I or a fission product sample from irradiated U.

7.0 References

Ambade, R. N.; Shinde, S. N.; Khan, M. S. A.; Lohar, S. P.; Vimalnath, K. V.; Joshi, P. V.; Chakraborty, S.; Pillai, M. R. A.; Dash, A. Development of a dry distillation technology for the production of ^{131}I using medium flux reactor for radiopharmaceutical applications. *J. Radioanal. Nucl. Chem.* **2015**, *303*, 451–467. DOI: 10.1007/s10967-014-3423-4

Bandyopadhyay, M.; Datta, S.; Sanyal, S. K. A mass transfer model for the hydrometallurgical extraction of Te(IV) by tri-n-butyl phosphate. *Hydrometallurgy,* **1996,** *43,* 175-185. DOI 10.1016/0304-386X(96)00003-5

Borisov, NB. Investigation of Gaseous Fractions of Radioactive Iodine. *Atomic Energy*, **2004**, Vol. 97, No. 5.

Caer, Le. Water Radiolysis: Influence of Oxide Surfaces on H2 Production. *Water*, **201**1, 235-253.

Choppin, G.; Liljenzin, J.; Rydberg, J. *Radiochemistry and Nuclear Chemistry*; Butterworth-Heinemann, Woburn, MA; 2002.

Decamp, C.; Happel, S. Utilization of a mixed-bed column for the removal of iodine from radioactive process waste solutions. *J. Radioanal. Nucl. Chem.* **2013**, *298*(2), 763-767. DOI: 10.1007/s10967-013-2503-1

Eichrom Technologies CL Resin product sheet; https://www.eichrom.com/eichrom/products/cl-resin/ (accessed 2022-06-13)

Eichrom Technologies Pb Resin product sheet; https://www.eichrom.com/eichrom/products/pb-resin/ (accessed 2022-06-20)

El-sweify, F. H.; Metwally, E. Comparative Study of the Extraction of Te(IV) from Various Aqueous Solutions Using Different Organic Diluents and Solvents. *Radiochemistry,* **2007,** *49(4),* 403-408. DOI: 10.1134/S1066362207060215.

Haefner, DR; Tranter, TJ. Methods of Gas Phase Capture of Iodine from Fuel Reprocessing Off-Gas: A Literature Survey, INL/EXT-07-12299, Idaho National Laboratory (2007); https://doi.org/10.2172/911962

Hassan, K.F.; Spellerberg, S.; Scholten, B.; Saleh, Z.A.; Qaim, S.M. Development of an ion-exchange method for separation of radioiodine from tellurium and antimony and its application to the production of ^{124}I via the ^{121}Sb(a,n)-process. *J. Radioanal. Nucl. Chem.* **2014**, *302*, 689–694. DOI: 10.1007/s10967-014-3270-3

Hoskins, JS; Karanfil, T; Serkiz, SM. Removal and sequestration of iodide using silver-impregnated activated carbon. *Environ. Sci. Technol.* **2002**, 36, 784-789

Huve, J; Ryzhikov, A, Nouali, H; Lalia, V; Aug'ed, G; Daou, TJ. Porous sorbents for the capture of radioactive iodine compounds: a review. *RSC ADV.*, **2018**, 8, 29248.

Joshi, PV; Jagadeesan, KC; Manolkar, RB; Mathakar, AR; Chirayil, V; Thakare, SV; Dash, A; Pillai, MRA. Production of 125I from Neutron Irradiation of Natural Xe Gas and a Wet

Distillation Process for Radiopharmaceutical Applications. *Ind. Eng. Chem. Res.* **2012**, 51, 8575−8582 https://doi.org/10.1021/ie301063h

Kang, SW; Yang, J; Yim, M. Examining Practical Application Feasibility of Bismuth-Embedded SBA-15 for Gaseous Iodine Adsorption, *Nuclear Technology*, **2020**, https://doi.org/10.1080/00295450.2020.1713680

Kahn, M.; Kleinberg, J. *Radiochemistry of Iodine, NAS-NS-3062*, National Academy of Sciences, 1977.

Koppenol, W.H., D.M. Stanbury, and P.L Bounds. Electrode potentials of partially reduced oxygen species, from dioxygen to water. *Free Radical Biology & Medicine*, **2010**, 317-322.

Korkisch, J. *Handbook of ion exchange resins*; CRC Press, Inc. 1989.

Leddicotte, G.W. *The Radiochemistry of Tellurium, NAS-NS-3038*, National Academy of Sciences, 1961.

Mincher, B.; Mezyk, S.; Martin, L. 2008. A Pulse Radiolysis Investigation of the Reactions of Tributyl Phosphate with Radical Products of Aqueous Nitric Acid Irradiation. *J. Phys. Chem. A* **2008**, *112*(28): 6275-6280. DOI: 10.1021/jp802169v

Mincher, B.; Modolo, G.; Mezyk, S. Review Article: The Effects of Radiation Chemistry on Solvent Extraction: 1. Conditions in Acidic Solution and a review of TBP Radiolysis. *Solvent Extr. and Ion Exch.*, **2009**, *27*, 1-25. DOI: 10.1080/07366290802544767

Nandanwar, SU; Coldsnow, K; Utgikar V; Sabharwall, P; Aston, DE. Capture of harmful radioactive contaminants from off-gas stream using porous solid sorbents for clean environment – A review. *Chemical Engineering Journal*, **2016**, 306, 369–381.

Nowak, M.; Nowak, Z. 1986. The Influence of Iodine on Radiolysis of PUREX-Solvent. *J. Radioanal. Nucl. Chem. Letter*s, **1986**, *103*, 141-152. DOI: 10.1007/BF02166560

NUCON Bulletin 11B31 – April 2006 (Revised January 2011) NUCON International, Inc

Pastina, B.; LaVerne J.A. Effect of Molecular Hydrogen on Hydrogen Peroxide in Water Radiolysis." *Journal of Physical Chemistry A*, **2001**, 9085-9322.

Pearson, J.; Nilsson, M. Radiolysis of Tributyl Phosphate by Particles of High Linear Energy Transfer. *Solvent Extr. and Ion Exch.*, **2014**, *32*, 584-600. DOI: 10.1080/07366299.2014.924305

Quintana, EE; Thyssen, SM. Determination of 129I in conifer samples around nuclear facilities in Argentina. *Journal of Radioanalytical and Nuclear Chemistry*, **2000**, 245(3), 545-550.

Riley, BJ; Vienna, JD; Strachan, DM; McCloy, JS; Jerden Jr., JL. Materials and processes for effective capture and immobilization of radioiodine: A review. *Journal of Nuclear Materials*, **2016**, 470, 307-32.

Sakurai, T.; Takahashi, A.; Ishikawa, N.; Komaki, Y. Interaction of Iodine with an Extractant of 30% TBP/70% n-Dodecane. *J. Nucl. Sci. Tech.*, **1995**, *32*(7), 664-670. DOI: 10.3327/jnst.32.664

Trevorrow, LE; Vandegrift, GF; Kolba, VM; Steindler, MJ. Compatibility of Technologies with Regulations in the Waste Management of H-3, I-139, C-14, and K-85. Part I. Initial Information Base, **1983**, ANL-88-57.

Watson, K; Ferre, MJ; Knight, N. Comparing a silver-impregnated activated carbon with an unmodified activated carbon for disinfection by-product minimization and precursor removal. *Science of the Total Environment*, **2016**, 542, 672–684.

Appendix A – Title

Use Body Text for paragraphs in this section. PNNL reports use http://www.chicagomanualofstyle.org/home.html for document style. Right-click and choose open hyperlink to view the style guide.

Pacific Northwest National Laboratory

902 Battelle Boulevard
P.O. Box 999
Richland, WA 99354

1-888-375-PNNL (7665)

www.pnnl.gov