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Project Title/Work Order Test Procedure for Anion Exchange Chromatography / K6JG6		EDT No. 119583 ECN No. NA

Name	MSIN	Text With All Attach.	Text Only	Attach./ Appendix Only	EDT/ECN Only
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NOV 14 1994

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1. EDT 119583

2. To: (Receiving Organization)  
PFP Process Engineering

3. From: (Originating Organization)  
Plutonium Process Support Labs.

4. Related EDT No:  
NA

7. Purchase Order No:  
NA

5. Proj/Prog/Dept/Div:  
WAE

6. Cog/Proj Engr:  
T. D. Cooper

9. Equip/Component No:  
NA

8. Originator Remarks:  
H/A

10. System/Bldg/Facility:  
234-5Z

12. Major Assm Dwg No:  
NA

13. Permit/Permit Application No.  
NA

14. Required Response Date:  
9/2/94

11. Receiver Remarks:

15. DATA TRANSMITTED

(A) Item No.	(B) Document/Drawing No.	(C) Sheet No.	(D) Rev No.	(E) Title or Description of Data Transmitted	(F) Impact Level	(G) Reason for Transmittal	(H) Originator Disposition	(I) Receiver Disposition
1	WHC-SD-CP-TP-079	-	0	Test Procedure for Anion Exchange Chromatography	SQ	1	1	1

16. KEY

Impact Level (F)	Reason for Transmittal (G)	Disposition (H) & (I)
1, 2, 3, or 4 see MRP 5.43 and EP-1.7	1. Approval 2. Release 3. Information 4. Review 5. Post-Review 6. Dist (Receipt Acknow. Required)	1. Approved 2. Approved w/comment 3. Disapproved w/comment 4. Reviewed no/comment 5. Reviewed w/comment 6. Receipt acknowledged

17. SIGNATURE/DISTRIBUTION (See Impact Level for required signatures)

(G) Reason	(H) Disp	(J) Name	(K) Signature	(L) Date	(M) MSIN	(J) Name	(K) Signature	(L) Date	(M) MSIN	(G) Reason	(H) Disp
1	1	Cog./Proj. Eng T. D. Cooper	<i>T.D. Cooper</i>	8/31/94	T5-12						
1		Cog./Proj. Eng. Mgr. C. S. Sutter	<i>C.S. Sutter</i>	PerTel	11/14/94						
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Authorized Representative Date for Receiving Organization

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*C.S. Sutter* PerTel 11/14/94  
Cognizant/Project Engineer's Manager Date

21. DOE APPROVAL (if required) Ltr No. \_\_\_\_\_  
 Approved  
 Approved w/comments  
 Disapproved w/comments

## RELEASE AUTHORIZATION

**Document Number:** WHC-SD-CP-TP-079, REV.0

**Document Title:** Test Procedure for Anion Exchange Chromatography

**Release Date:** November 14, 1994

**This document was reviewed following the  
procedures described in WHC-CM-3-4 and is:**

**APPROVED FOR PUBLIC RELEASE**

**WHC Information Release Administration Specialist:**

  
\_\_\_\_\_  
Kara M. Broz

November 14, 1994  
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SUPPORTING DOCUMENT		1. Total Pages <sup>30</sup> 20 <i>TPC</i> 1/14/94
2. Title Test Procedure for Anion Exchange Chromatography	3. Number WHC-SD-CP-TP-079	4. Rev No. 0
5. Key Words Plutonium, Plutonium Finishing Plant, PFP, Plutonium Nitrate, Ion Exchange, Anion Exchange, Absorbers, Degradation, Thermal Stability, Exchange Capacity <i>WHC 11/14/94</i>	6. Author Name: T. D. Cooper <i>T. D. Cooper</i> Signature Organization/Charge Code 8E120/ K6JG6	
<b>APPROVED FOR PUBLIC RELEASE</b>		
7. Abstract Plutonium from stored nitrate solutions will be sorbed onto anion exchange resins and converted to storable plutonium dioxide. Useful information will be simultaneously gained on the thermal stability and ion exchange capacity of four commercially available anion exchange resins over several years and under severe degradative conditions. This information will prove useful in predicting the safe and efficient lifetimes of these resins.		
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9. Impact Level SQ		

WHC-SD-CP-TP-079

Rev. # 0

Test Procedure  
for Anion Exchange  
Chromatography

Prepared by  
Thurman Cooper

Aug. 24, 1994

**MASTER**

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## 1.0 INTRODUCTION

Some of the plutonium in the Plutonium Finishing Plant (PFP) is stored as stable plutonium dioxide ( $\text{PuO}_2$ ) in the vaults, while other plutonium is contained in the plant as nitrate solutions, sludges, oxide, oxalates, and numerous other forms. All plutonium not already converted to sintered high-fired oxide should be viewed as potentially-reactive material and not suitable for a long-term storage mission that might exceed 50 years.

Of particular concern are the 2,200 L of plutonium nitrate solutions containing 16.8 kg of plutonium. Some of these solutions are stored in 10-L containers. The 10-L containers have a stainless steel outer shell and a plastic inner bottle containing the plutonium nitrate-nitric acid solution. Because of chemical aging and radiolysis, these plastic inner bottles are potentially brittle. While X-ray analysis shows no evidence that these bottles have failed, it is considered wise to (1) remove these solutions from the 10-L containers before failure; and (2) convert the plutonium nitrate to solid  $\text{PuO}_2$  as a final storage form.

## 2.0 PLUTONIUM SEPARATION BY ANION EXCHANGE CHROMATOGRAPHY

It is desirable to concentrate the plutonium from the original nitrate solutions by a simple and efficient technique. Anion exchange chromatography has been used for 30 years on both the bench and plant scale to complete this task. Moreover, anion exchange is internationally recognized as the simplest and most efficient method for accomplishing this task.

If anion resins were totally stable and not susceptible to chemical and/or radiolytic damage, there would be no need for further evaluation or development. Because this is not the case, it is important that we understand these phenomena in detail.

Typically, anion exchange resins are viewed as three-dimensional matrices composed of styrene or pyridinium rings linked by methylene groups. A certain proportion of the rings are functionalized to contain a positively charged quaternary ammonium or pyridinium group that has the capacity of absorbing negatively charged anions from aqueous solutions.

These resins are not immune from chemical or radiolytic degradation. The results of such degradation are as follows.

- Delink the 3-dimensional matrix through bond rupture at the methylene sites.
- Add hydroxyl groups to the resin at the site of ruptured bonds.
- Defunctionalization as the active functional group is reacted, which results in lowering the resin exchange capacity.

- Degrade the ring structures to smaller, simpler, and more highly oxidized molecules such as alcohols, aldehydes, and organic acids.

This degradation has the ultimate effect of changing the chemical reactivity of the resin as daughter products accumulate and reducing the number of active ion exchange sites remaining on the three-dimensional matrix. Although other studies have been performed on the degradation of anion exchange resins, none exhaustively studied these phenomena over large periods of time so that the operational lifetimes can be adequately predicted. It is the intent of this test plan to define the operational life of the resins when degraded over large periods of time.

### 3.0 TEST ITEMS

Macroreticular anion exchange resins include (1) Lewatit MP 500 SK; (2) Reillex HPQ; (3) Dow MSA-1; and (4) Amberlite IRA-9000.

### 4.0 GENERAL DESCRIPTION OF TESTS

Four anion exchange resins will be tested to determine the distribution coefficients, selectivity coefficients, thermal stability, and ion-exchange capacity of each material. These characteristics will also be correlated to the natural alpha radiation dose, hydrogen ion activity, nitrate ion activity, and exposure time. These tests may be divided into the following sections.

**Batch Experiments.** Sixteen experiments will be run for each anion exchange material to study the effects of chemical and radiolytic degradation for time periods varying between 0.5 months to 2 years. These parametric experiments further described in Section 10.4 will be conducted in 1-L sealable glass vessels. Because four organic ion exchangers are being tested, this will result in a total of 64 batch experiments. Once a month, 5 g of resin will be withdrawn and tested for distribution coefficients, ion selectivity, ion exchange capacity, and thermal stability.

**Column Experiments.** All four ion exchange materials will be tested (in duplicate column experiments) for their performance under approximate plant conditions. Of particular interest is their performance during repeated load and unload cycles. In these column experiments, the resin columns will be loaded to breakthrough capacity and unloaded repeatedly using standard flowsheet conditions. Once a month a 5-g resin sample will be removed and tested for distribution coefficients, ion exchange capacity, and thermal stability.

## **5.0 TEST CONDITION LIMITS**

Anion exchange batch and column experiments will be performed at room temperature. Individual samples of each experiment will be obtained as a function of time and heated up to 360 °C to study the thermal stability of these resins.

## **6.0 INSTRUMENTS AND CALIBRATION**

The following instruments are required for this procedure.

- Packard liquid scintillation counter
- DTA-TGA instrument at the 222-S Laboratory
- Induction coupled plasma (ICP) instrument
- Ion chromatograph instrument.

These instruments are calibrated on a schedule and in a manner as dictated by approved procedures.

## **7.0 FACILITIES, EQUIPMENT, AND MATERIALS TO BE USED**

### **7.1 FACILITIES**

The facilities to be used are the sash hoods and glove boxes in Room 179 and the sash hoods in Room 187 of the 234-5 Building, 200 West Area.

### **7.2 EQUIPMENT REQUIRED**

The following equipment is required.

- 64 1-L sealable glass vessels
- Eight glass chromatographic columns

- Ionic potential recorder
- Titration burettes.

### 7.3 MATERIALS

The following materials are included.

- Deionized water
- $\text{Pu}(\text{NO}_3)_4$  storage solutions
- Anion exchange resins
- Ultima Gold Cocktail
- Common laboratory reagents such as aluminum nitrate  $\text{Al}(\text{NO}_3)_3$ , nitric acid  $\text{HNO}_3$ , and sodium hydroxide (NaOH).

## 8.0 SAFETY

### 8.1 CRITICALITY SAFETY AND RADIOLOGICAL SAFETY

Safety considerations include criticality and radiological safety, which are both important aspects of glove box and sash hood operations. These safety considerations will be assured by strict adherence to CPS-L-114-00010, -00020, -00030, -00040, and -01900, and to the building Radiation Work Permits.

### 8.2 HANDLING CHEMICALS

All chemicals will be handled in accordance with (1) the Westinghouse Hanford Company *Chemical Hygiene Plan* (WHC-SD-CP-HSP-001) and (2) the specific instructions contained in Appendix A.

### 8.3 REAGENT CHEMICAL SAFETY

See Appendix A.

## **9.0 NO SPECIAL MAINTENANCE REQUIRED AND NO FAILURES ANTICIPATED**

Interruptions in access to the job site will not lead to process or safety compromises because the tests can be left unattended without significant safety concerns. No special maintenance is required for these experiments and no failures of equipment or instruments are anticipated.

## **10.0 TEST DATA**

### **10.1 DISTRIBUTION COEFFICIENTS**

The distribution coefficients may be defined as follows.

- $K_d = \frac{\text{TRU element concentration in exchanger (mmol/g)}}{\text{TRU element concentration in solution (m mol/g)}}$

For each of these exchange materials, the distribution coefficients will be determined as a function of the nitrate ion activity and the solution ionic strength.

### **10.2 SELECTIVITY COEFFICIENT**

The selectivity coefficient measures the affinity of each anion for the exchange material as compared to the affinity of the nitrate ion. By comparing selectivity coefficients, one may gauge the selectivity of the material for each anion in solution.

The selectivity coefficient will be measured for the (1) plutonium nitrate anion complex; (2) first, second, and third row transition metal nitrate complexes; and (3) rare earth nitrates.

### **10.3 ION EXCHANGE CAPACITY**

The ion exchange capacity of these resins will also be measured as a function of the same independent parameters.



#### 10.4 THERMAL STABILITY

The thermal stability of these four macroreticular anion exchange resins (when reacted with HNO<sub>3</sub>) will be measured. Independent parameters for these tests will include (1) absorbed alpha radiation dose; (2) hydrogen ion activity; (3) nitrate ion activity; and (4) exposure time.

#### 10.5 CHEMICAL STABILITY

A parametric study will be performed to identify the important independent variables or combinations thereof. Each independent variable will be tested at 2 levels: high and low. Values for each level are recorded in Table 1.

Table 1. Independent Variable Settings.

Independent variable	Low setting	High setting
Plutonium loading	10% Saturation	Saturation
Hydrogen ion activity	0.5 Molar	7 Molar
Nitrate ion activity	0.5 Molar	7 Molar
Time	0.5 Months	24 Months

Sixteen permutations exist for these independent variable settings and each permutation will result in a separate experiment.

#### 10.6 OPERATIONAL HISTORY

The changes in distribution coefficients, ion selectivities, resin thermal stability, and ion exchange capacity will also be measured for each of these resins in response to the number of months of continuous and typical use. This measures the response of the resin to dynamic flow conditions, load and unload cycles, and changing chemical environments. The resin will be sampled on a monthly basis and the sampling program will continue for a two-year period.

#### 11.0 PERSONNEL REQUIRED

For this operation, only normal Plutonium Process Support Laboratory personnel are required.

## 12.0 WITNESSES REQUIRED

For this operation, no witnesses are required. Nuclear Safety and the PFP Criticality Representative will be accorded the opportunity to witness the tests.

## 13.0 PROCEDURE FOR TESTS

### 13.1 PROCEDURE FOR DETERMINING THE DISTRIBUTION COEFFICIENT

For each of the anion exchange resins, 0.2 g in the nitrate form will be equilibrated with 20 cm<sup>3</sup> of the mixed solution containing a TRU element and 7 molar HNO<sub>3</sub> with intermittent stirring at 25 °C. Plutonium will be determined by alpha counting. The uptake will be calculated as the difference between the initial and final aqueous concentrations. The concentration of non-radioactive elements will be determined by spectral adsorption such as ICP.

### 13.2 PROCEDURE FOR DETERMINING THE SELECTIVITY COEFFICIENT

The selectivity coefficient  $K_H^M$  will be determined in the same manner as the distribution coefficient except that the concentration of nitrate will also be measured in both the aqueous and ion exchange materials. This will allow a comparison between the affinity of the given anion and the affinity of the nitrate ion for the exchange material as in the equation:

$$K_H^M = \frac{X_M^*}{X_H^{*n}} \frac{X_H^n}{X_M} \frac{\gamma_H^n}{\gamma_H} n(TN)^{n-1}$$

where:

$X_M^*$  = the ionic fraction of metal ion in the anion resin

$X_H^{*n}$  = the ionic fraction of nitrate in the anion resin raised to the nth power.

$X_H^n$  = The ionic fraction of nitrate in the aqueous solution raised to the nth power

$X_M$  = The ionic fraction of metal ion in the aqueous solution

$\gamma_H^n$  = The activity coefficient of nitrate in the aqueous solution raised to the nth power

$\gamma_M$  = The activity coefficient of metal ion in the aqueous solution.

n = The ionic charge on the metal ion

TN = The total normality of the solution

The selectivity coefficient is fundamentally more important than the distribution coefficient because the distribution coefficient is an empirical factor that cannot be correlated to the remaining system parameters whereas the selectivity coefficient can as in:

$$\log K_H^M = K_H^M (X_M^{*-O}) + 2C X_n^*$$

where C has a negative value and is called the Kielland coefficient.

### 13.3 PROCEDURE FOR THE PARAMETRIC STUDY

For each resin type, 16 parametric experiments shall be performed. Each experiment shall consist of first determining the chloride ion exchange capacity of each resin. Then 300 g of each resin will be equilibrated with the desired amount of plutonium and slurried into a 1-L sealable glass container. Secondly the required amounts of acid and nitrates will be added. Finally, the resin will be tested for distribution coefficients, ion selectivity, thermal stability, and ion exchange capacity as a function of time. The chloride ion exchange capacity will be determined for each sample by saturating the resin with chloride and determining the amount of chloride taken up by the resin through argentometric analysis. Thermal stability will be tested on the 222-S Laboratory's DTA-TGA instrument. Heat flow to or from the sample will be determined as a function of reaction temperature using DTA techniques. The heat flow will be reported in calories per gram of resin. The TGA technique will be used to determine the weight change of the sample as a function of reaction temperature. These tests will be repeated once a month for 2 years.

#### **14.0 DISPOSITION OF TEST ITEMS REQUIRED**

All plutonium nitrate shall be converted as a minimum to stable oxide or preferably to pressed and sintered  $\text{PuO}_2$  pellets and shall be stored in the vaults. All aqueous waste materials shall be discharged to tank farms. Resin residues shall be ashed, leached to recover plutonium, dried, and discharged as low-level solid wastes.

#### **15.0 REPORTS REQUIRED**

A technical report document will be completed to document the results of these experiments.

#### **16.0 DATA SHEETS MAINTAINED**

Data will be recorded in a controlled bound notebook by the principal investigating scientist.

**APPENDIX A**

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## APPENDIX A

### A.1 STANDARD LABORATORY PROCEDURES

#### ANION EXCHANGE COLUMN EXPERIMENTS

**Column Description.** An anion absorption column 60-cm long and 5 cm in diameter is prepared with a fritted glass support, a standard burette stopcock valve at the bottom, and a 5-cm long pointed tip that has a 2-mm diameter opening in the end.

**Resin Preparation.** A macroreticular anion exchange resin shall be used as the solid phase chromatographant. The resin shall be prepared by suspending 1 kg in 4 L of water, rapidly swirling the suspension, and letting it settle for several minutes. The solution is decanted when it is obvious that the solid beads have settled and the broken fragments are still in suspension. This process is repeated a second time. Next, the resin is suspended in water and transferred to the column. An excess of water should cover the resin at all times.

**Resin Conditioning.** The resin is conditioned with 2 column volume of 7 M HNO<sub>3</sub> (prepared by diluting 450 ml of con. HNO<sub>3</sub> into 1 L of distilled water). The flow rate is adjusted to not exceed 5 ml/minute.

**Feed Preparation.** Plutonium nitrate feed will be removed from 10-L containers by operations personnel and transferred to the laboratory in 4-L plastic containers. The volume of the plutonium feed solution and the plutonium mass must be within the permissible range provided by the criticality specification for the work site.

The plutonium feed stream will be centrifuged and then filtered with a 5 micron filter to remove undesired solids. Following filtration, the feed stream will be saturated with aluminum nitrate. This provides part of the nitrate ion required to form the negatively charged hexanitrate plutonium complex  $[\text{Pu}(\text{NO}_3)_6]^{2-}$  and also serves as a complexer for other ligands that might interfere. A third benefit is that the highly charged aluminum ion raises the ionic strength of the solution and reduces the activity of water, thereby increasing the equilibrium concentration of the plutonium-resin complex.

The total nitrate activity must be adjusted to 7 molar. This is to ensure that the hexanitrate complex forms in adequate concentration for anion exchange chromatography. This requirement is met by summing the nitrate contributed by aluminum nitrate (3 N), and nitrate from nitric acid and other inorganic nitrate salts.

The hydrogen ion concentration must be maintained above 1.0 molar to stabilize plutonium in the quadrivalent oxidation state.

**Valence Adjustment.** To absorb efficiently on an anion column, plutonium must be in the +4 oxidation state. If PU(V) or Pu(VI) is in the feed stream, reduction to Pu(III) can be accomplished by using a reductant such as hydrogen peroxide. The concentration of penta or hexavalent plutonium for each feed solution will be determined spectrophotometrically. After adjusting the peroxide/ $\text{Pu}^{+4}$  ratio to the stoichiometric point plus 10%, 10 g/L of sodium nitrite is added to stabilize Pu(4), and the solution is heated to 80 °C for 1 hour to allow the nitric acid to oxidize PU(III) to Pu(IV).

**Loading the Column.** All column operations shall be performed in a glove box. The filtrate may be added to the column and loaded at the rate of 5 ml/min. The plutonium anionic complex will load as a colored band. This band can be tracked visually as the column progressively loads and is eventually stripped. In no case should the column be left loaded or in contact with 7 M nitrate for more than 8 hours before being stripped.

**Stripping the Column.** After loading, the column should be washed with 2 column volumes of 7 M nitric acid to remove all contaminants and then eluted with three column volumes of 0.25 M  $\text{HNO}_3$  (prepared by diluting 16 ml of con  $\text{HNO}_3$  into 1 L of distilled water).

**Storage Conditions.** After stripping, the column can be stored in 0.5 M  $\text{HNO}_3$ . After use, the column should be stored with at least 7.6 cm (3 in.) of fluid over the resin to insure the stability of the resin bed and to prevent air entering the column. If air enters the column, the resin must be reslurried to expel the air before reuse.

## A.2 STANDARD LABORATORY MATERIAL HANDLING PROCEDURES

### ACIDS OR STRONG BASES

**Clothing Requirements.** These include the following: coveralls, rubber or plastic apron, rubber gloves, face shield or safety goggles, shoes with non-skid soles, and reagent bottles to be in an approved carrier.

**Ventilation Requirements.** All acids or strong bases will be mixed or reacted in a glove box or sash hood.

**Transportation and Use.** Concentrated acids or bases must be transported to a sash hood or glove box in an approved carrier and must be used within the confines of that facility. Acids or bases must be added to water in the dilution step. Acids or bases must not be mixed with any reagents except as directed and in the exact sequence and amounts stated in the work plan. Care must be exercised to prevent the external or internal contamination of persons with concentrated acids or bases.



The dilution procedure is as follows.

- Affix oxidizer/acid or base labels to plastic bottles.
- Don clothing, acid apron, rubber gloves, and face shield or safety goggles.
- Place H<sub>2</sub>O in volumetric flask.
- Add conc. acid or base.
- Dilute to volume.
- Invert and shake 10 times. Shaking is to be done gently with a rocking motion. It will be demonstrated by the cognizant chemist before being performed by the technicians.
- Transfer solution to plastic bottle.
- Rinse volumetric flask and dispose of rinsate as hazardous waste.

**Storage.** Store in an approved acid or base storage cabinet. All such materials must be listed on an attached inventory sheet.

#### **DRY CHEMICALS**

**Ventilation Requirements.** All handling and reactions must be performed in a glove box or sash hood.

**Clothing Requirements.** Rubber gloves and a laboratory coat are the minimum clothing requirements. Wash hands thoroughly after handling.

**Eye Protection.** Chemical safety goggles or glasses shall be worn when handling corrosive materials.

**Storage.** Store in tightly capped plastic bottle in chemical storage area when not in use.

#### **ORGANIC CHEMICALS**

**Clothing Requirements.** A full suit of protective clothing shall be worn when handling any organic chemical that is not contained in a sealed canister or confinement device such as a glove box or sash hood. Rubber gloves shall always be worn to protect the hands.

**Ventilation Requirements.** All handling and reactions must be performed in a glove box or sash hood.

**Eye Protection.** Chemical safety goggles or glasses shall always be worn when handling organic chemicals.

**Storage.** Store in tightly capped reagent bottles in approved chemical or solvent storage areas when not in use.

### **GENERAL FIRST AID INSTRUCTIONS**

**Inhalation.** Remove from exposure area to fresh air immediately. If breathing has stopped, give artificial respiration. Do not inhale the victim's exhaled breath. Call 911 for medical assistance.

**Skin Contact.** Remove contaminated clothing and shoes immediately. Wash skin with large amounts of water. Call 911 for medical assistance.

**Eye Contact.** Wash eyes immediately with large amounts of water, occasionally lifting upper and lower lids, until no evidence of chemical remains (at least 15 to 20 minutes). Continue irrigating and call 911 for medical assistance.

**Ingestion.** For alkali or acid ingestion, immediately give water to drink. For organic chemical/material ingestion, allow natural vomiting to occur but do not induce vomiting. Call 911 for emergency assistance.

### **A.3 CHEMICAL REAGENT SAFETY**

The following information was compiled from individual MSDSs, *The Dangerous Properties of Industrial Materials* (Sax 1984), and several other sources. Furthermore, revisions to these sources and future information that becomes available during the course of these experiments should be consulted regularly.

#### **A.3.1 Nitric Acid (MSDS 1384)**

**Chemical Formula.**  $\text{HNO}_3$

**Synonyms.** Aqua fortis, azotic acid, hydrogen, nitrate, nitryl hydroxide, nital.

**Properties.** These include the following.

- Clear to yellowish liquid
- Melting point:  $-42\text{ }^\circ\text{C}$
- Boiling point:  $83\text{ }^\circ\text{C}$

- Density: 1.503 g/cc.

**General Description.** Nitric acid is flammable by chemical reaction with most organic materials and other reducing agents and is a powerful oxidizing agent. It is hypergolic in many of its reactions (needs no heat source to propagate an explosion). Nitric acid will react with water or steam to produce heat and toxic and corrosive fumes, to fight fire, use water. When heated to decomposition (above 150 °C), it emits highly toxic fumes of nitrogen oxides and hydrogen nitrate.

**First Aid Instructions.** For external contamination of clothes, skin, eyes, or hair wash with copious quantities of water. For ingestion, drink several glasses of water. Call 911 for emergency assistance.

**Medical Description.** Nitric acid is a human poison by unspecified routes. An experimental teratogen (damages DNA). Experimental reproductive effects. Corrosive to eyes, skin, mucous membranes, and teeth. Causes upper respiratory irritation which may seem to clear up only to return in a few hours and more severely.

**Hazardous Nitric Acid Reactions.** In these experiments, the reaction of concern is with organic ion exchange resins or degradation products therefrom. Violent reactions will be avoided by limiting the mass of reactive organics that will contact significant nitrate concentrations.

### A.3.2 Sodium Hydroxide (MSDS #1105)

**Chemical Formula.** NaOH

**Synonyms.** Caustic soda, lye, soda lye, sodium hydrate, white caustic, ascarite

**Properties.**

- White, deliquescent pieces, lumps or sticks. In solution a clear liquid and may be viscous if concentrated.
- Melting point: 159 °C
- Boiling point: 754 °C
- Density: 2.12 g/cc

**General Description.** A white solid, either as lumps, flakes, pieces or sticks, or a clear, viscous aqueous solution of same. Very caustic, it reacts vigorously and at times violently with many acidic substances. Extremely hazardous to eyes, skin, or upon internal ingestion.

**Medical Description.** Poison by intraperitoneal route. Moderately toxic by ingestion. Mutagenic data. A corrosive irritant to skin, eyes and mucous membranes. This material, both solid and in solution, has a markedly corrosive action upon all body tissue causing burns and frequently deep ulceration, with ultimate scarring. Mists, vapors, and dusts of this compound cause small burns, and contact with the eyes rapidly causes severe damage to the delicate tissue. Ingestion causes very serious damage to the mucous membranes or other tissues with which contact is made. It can cause perforation and scarring. Inhalation of the dust or concentrated mix can cause damage to the upper respiratory tract and to lung tissue, depending upon the severity of the exposure. Thus, effects of inhalation may vary from mild irritation of the mucous membranes to a severe pneumonitis.

**Hazardous Chemical Reactions.** A review of the hazardous chemicals database reveals no uniquely hazardous sodium hydroxide reactions in these experiments. The primary chemical reaction hazard to avoid will be the mixing of concentrated sodium hydroxide with concentrated nitric acid.

### A.3.3 Ultima Gold Cocktail (MSDS #21700)

**Chemical Formula.** Mixture of organic compounds

**Synonyms.** None

**Properties.**

- Clear blue-violet fluorescent liquid with mild odor.
- M.P. 30 °C
- B.P. 295 °C
- S.G. 0.960

**General Description.** Clear organic liquid which is a blend of alkylnaphthalene with scintillators PPO and bis-MSB and emulsifiers. Contains a mildly irritating solvent alkylnaphthalene. Avoid contact with eyes and skin, prolonged breathing of vapor. Avoid sparks and open flame. Keep tightly closed. Protect from light. Prolonged contact may cause slight irritation of eyes, skin and mucous membranes. May cause nausea, diarrhea, or vomiting if ingested. No chronic effects are known.

**Hazardous Chemical Reactions.** As with most organics, mixing with strong oxidizers such as concentrated perchloric or nitric acid can result in an explosive/flammable reaction.

**A.3.4 Lewatit MP 500 Anion Exchange Resin (MSDS #25894)**

**Chemical Formula.**  $(C_8H_9N^+)_x$

**Synonyms.** None

**Properties.**

- Solid 3 mm beads of resinous texture and brown-gold color
- M.P. Not determined
- B.P. Not determined
- Density 1.1g/ml

**General Description.** This anion exchange resin is a high molecular weight pyridinium polymer. At room temperature it is considered a chemically stable organic compound with a low vapor pressure. At elevated temperatures ( $>204\text{ }^\circ\text{C}$ ) decomposition may occur. Rapid exothermic reactions have occurred at temperatures in excess of  $150\text{ }^\circ\text{C}$  and in the presence of strong oxidizers. Decomposition products are CO, CO<sub>2</sub>, and pyridine. Despite the possibility of exothermic reactions, with appropriate safety controls, these resins are used advantageously and quite safely in laboratories and in industry on a worldwide basis.

**A.3.5 Reillex HPQ Anion Exchange Resin (MSDS #35852)**

**Chemical Formula.**  $(C_8H_9N^+)_x$

**Synonyms.** 1-methyl-4-vinylpyridine/divinylbenzene

**Properties.**

- Solid 3-mm beads of resinous texture and brown-gold color
- M. P. = Not determined
- B. P. = Not determined
- Density = 1.1g/ml.

**General Description.** This anion exchange resin is a high molecular weight pyridinium polymer. At room temperature it is considered a chemically stable organic compound with a low vapor pressure; at elevated temperatures ( $>204\text{ }^\circ\text{C}$ ) decomposition occurs. Rapid exothermic reactions have occurred at temperatures in excess of  $150\text{ }^\circ\text{C}$  and in the presence

of strong oxidizers. Decomposition products are CO, CO<sub>2</sub>, and pyridine. Despite the possibility of rapid exothermic reactions, with appropriate safety controls, these resins are used advantageously and safely in laboratories and in industry on a worldwide basis.

### **A.3.6 Dowex MSA-1 Anion Exchange Resin (MSDS #19902)**

**Chemical Formula.** (C<sub>11</sub>H<sub>16</sub>N<sup>+</sup>)<sub>x</sub>

**Synonyms.** 1-quaterammonium-4-vinylbenzene/divinylbenzene

#### **Properties.**

- Solid 3-mm beads of resinous texture and brown-gold color
- M.P. = Not determined
- B.P. = Not determined
- Density = 1.1 g/ml.

**General Description.** This anion exchange resin is a high molecular weight benzene/divinylbenzene polymer. At room temperature it is considered a chemically stable organic compound with a low vapor pressure. Decomposition occurs at elevated temperatures (>204 °C). Rapid exothermic reactions have occurred at temperatures in excess of 150 °C and in the presence of strong oxidizers. Decomposition products are CO, CO<sub>2</sub>, and pyridine. Despite the possibility of rapid exothermic reactions, with appropriate safety controls, these resins are used advantageously and safely in laboratories and in industry on a worldwide basis.

### **A.3.7 Amberlite IRA-9000 Anion Exchange Resin**

**Chemical Formula.** (C<sub>11</sub>H<sub>16</sub>N<sup>+</sup>)<sub>x</sub>

**Synonyms.** 1-quaterammonium-4-vinylbenzene/divinylbenzene

#### **Properties.**

- Solid 3-mm beads of resinous texture and brown-gold color
- M.P. = Not determined
- B.P. = Not determined

- 
- 
- Density = 1.1g/ml.

**General Description.** This anion exchange resin is a high molecular weight quaterammonium benzene/divinylbenzene polymer. At room temperature it is considered a chemically stable organic compound with a low vapor pressure. At elevated temperatures (>204 °C) decomposition occurs. Rapid exothermic reactions have occurred at temperatures in excess of 150 °C and in the presence of strong oxidizers. Decomposition products are CO, CO<sub>2</sub>, and pyridine. Despite the possibility of rapid exothermic reactions, with appropriate safety controls, these resins are used advantageously and safely in laboratories and in industry on a worldwide basis.

**A.3.8 Safely Using Anion Exchange Resins.** The following facts must be recognized when dealing with ion exchange resins.

- Resins are organic chemicals that will chemically degrade if subjected to a strong oxidizing environment, a high radiation field, or to high temperature.
- Degradation alone does not imply a severe safety threat, however degraded resins mixed with strong oxidizers may react rapidly.
- Resins (whether confined or unconfined) may react with oxidizers, however they will not detonate as a high explosive. When confined, and undergoing a rapid exothermic reaction, the temperature and pressure may climb until the sealed container bursts and the resulting release of heat and steam is termed an explosion. The safety measures required for using anion exchange resins are as follows:
  - Minimize the concentration of strong oxidizers that contact the resins. The maximum nitric acid concentration used in an operating column will be 7 Molar.
  - Minimize the time allowed for strong oxidizers on the column. The nitrate concentration in stored columns will not exceed 1/2 molar.
  - Minimize the integrated radiation dose absorbed by the resin. Resins are typically considered completely degraded when the integrated radiation dose exceeds  $5 \times 10^8$  Rads.

Consequently, the radiation dose on operating columns will be limited to  $10^6$  Rads.

The radiation dose will be estimated from the loading history of the columns (i.e., amount of plutonium loaded on the column and exposure time.) A cumulative log of radiation exposure will be kept for each column. The resin will be changed before the dose limit is reached.

A second safety measure is the use of active or passive cooling systems. In these experiments, the column inner diameter will be limited to 5.1 cm. This will insure that the heat conduction path length is relatively short and therefore minimize the cross sectional temperature differential.

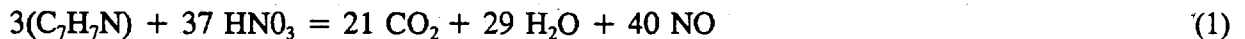
The third safety measure is to design the columns with large openings or pressure relief plugs so that in the event of a pressure excursion, most of the resin is ejected into the glove box. The columns used in this experiment are open at the top.

A fourth safety measure is to change the resins periodically to prevent the use of degraded resins. The periodicity for change is a function of the total exposure to oxidizers and radioactivity integrated over time.

Radiation exposure should be limited to 5 million rads. Chemical degradation is more difficult to measure or limit because it is a function of time, temperature, and reagent concentrations. An object of this experiment is to find a rational basis for limiting resin chemical degradation.

A fifth safety measure is to limit the mass of dry resin. Limiting the mass, restricts the total heat and gas which could be released if an exothermic excursion occurs.

Pyridinium resin-nitric acid reaction that maximizes reaction enthalpy is calculated as follows:



The heat of reaction is calculated as follows:

$$H_r = H_{\text{products}} - H_{\text{reactants}} \quad (2)$$

$$H_{CO_2} = -94.05 \text{ Kcal/mole}$$

$$H_{H_2O} = -57.80$$

$$H_{NO} = +21.56$$

$$H_{C_7H_7N} = +7.12$$

$$H_{HNO_3} = -49.37$$



$$H_r = \{[21(-94.05) + 29(-57.8) + 40(21.56)] - [3(7.12) + 37(-49.37)]\}$$

$$H_r = -983.52 \text{ kcal/3 mole} = -328 \text{ kcal/mole}$$

This heat will be absorbed by (1) the glove box structure; (2) the atmosphere in the glove box; (3) the aqueous phase in the ion exchange column; and (4) converting some of the liquid water to water vapor.

The total volume of the glove box is 14,140 L so the moles of atmospheric gas are:

$$14,140 \text{ L} / 24.46 \text{ L/mole} = 578 \text{ moles of gas}$$

The heat absorbed by this air is given by:

$$\frac{578 \text{ moles air} \times 7.0 \text{ cal} \times (T - 25) \text{ }^\circ\text{C}}{\text{g-mole} \cdot \text{ }^\circ\text{C}} = H_{\text{atm}} \quad (3)$$

Let  $M_{\text{H}_2\text{O}}$  be the moles of liquid water in the column,

$$M_{\text{H}_2\text{O}} = 60 \text{ cm} \times 3.1412 \times (1.25 \text{ cm})^2 / 18 \text{ cm}^3/\text{mole} \quad (4)$$

$$= 16.36 \text{ moles liquid water}$$

The heat absorbed by the liquid water is given by:

$$\frac{16.36 \text{ g-moles} \times 18 \text{ cal} \times (T - 25) \text{ }^\circ\text{C}}{\text{g-mole} \cdot \text{ }^\circ\text{C}} = H_{\text{water}} \quad (5)$$

More heat will be absorbed as the products of the oxidative reaction are heated from ambient to the equilibrium temperature. Because 36 moles of gas are produced per mole of resin reacted.

$$\frac{M_{\text{resin}} \times 36 \text{ g-moles gas} \times 7.0 \text{ cal} \times (T - 25) \text{ }^\circ\text{C}}{m_{\text{resin}} \text{ g-mole gas} \cdot \text{ }^\circ\text{C}} = H_{\text{prodgas}} \quad (6)$$

The liquid water which changes to a vapor absorbs heat

$$\frac{(M_{\text{steam}} \times 9720 \text{ cal})}{\text{g-mol}} + \frac{(M_{\text{steam}} \times 7.2 \text{ cal} \times (T - 25) \text{ }^\circ\text{C})}{\text{g-mole} \cdot \text{ }^\circ\text{C}} = H_s \quad (7)$$

$$\text{so } H_r = H_{\text{atm}} + H_{\text{water}} + H_{\text{prodgas}} + H_s \quad (8)$$

now three independent variables are contained in Equation 8:

- The number of moles of resin  $M_{\text{resin}}$

- The equilibrium temperature T
- The number of moles of steam  $M_{\text{steam}}$

A value is assigned to  $M_{\text{resin}}$  and it is assumed all of the liquid water is converted to steam. If the equilibrium temperature is above 100 °C the assumption is considered good. If the equilibrium temperature is not above 100 °C, the molar concentration of water vapor at the equilibrium temperature is substituted for  $M_{\text{steam}}$  in Equation 7. After a few iterations, convergence was achieved.

This calculation was performed with the Mathematica software program and 2.55 moles of resin may be oxidized instantaneously to bring the glove box up to its allowed over pressure limit of 10 psig.

This calculation represents an extreme limiting case because we have assumed that oxidation is both complete and instantaneous. In fact, an open 5-cm diameter column would eject its contents upon internal pressurization. We estimate that less than 5% oxidation would occur before the reaction mixture would eject and be immediately quenched by the cool glove box surfaces.

By this argument we believe that 2.55/0.05 moles of resin (or 6,069 g) can be handled safely in an open column. The columns will be designed to only hold 1,250 g of resin or less to preclude the accidental overcharge of a column.