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APPROVED FOR PUBLIC RELEASE

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7. Abstract

The purpose of this test plan is to demonstrate the synthesis of inorganic antimonate ion exchangers and compare their performance against the standard organic cation exchangers. Of particular interest is the degradation rate of both inorganic and organic cation exchangers. This degradation rate will be tracked by determining the ion exchange capacity and thermal stability as a function of time, radiation dose, and chemical reaction.

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**Test Procedure
For Cation Exchange
Chromatography**

**Prepared by
Thurman Cooper**

Aug. 24, 1994

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LIST OF TERMS

PFP	Plutonium Finishing Plant
L	Liter
Kg	Kilogram
ICP	Induction coupled plasma instrument
RWP	Radiation Work Permit

TEST PROCEDURE FOR CATION EXCHANGE CHROMATOGRAPHY

1.0 INTRODUCTION

Some of the plutonium in the Plutonium Finishing Plant (PFP) is stored as stable plutonium dioxide (PuO_2) in the vaults, while other plutonium is still contained in the PFP 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 liters (L) of plutonium nitrate solutions containing 16.8 kilograms (Kg) of plutonium. Some of these solutions are stored in 10-L containers. The 10-L containers have an outer shell of stainless steel and contain a plastic inner bottle that contains the plutonium nitrate-nitric acid solution. Because of chemical aging and radiolysis, these plastic inner bottles are potentially brittle. X-ray analysis shows no evidence that these bottles have failed; however, it is considered wise to remove these solutions from the 10-L containers before failure, and to convert the plutonium nitrate to solid PuO_2 as a final storage form.

2.0 PLUTONIUM SEPARATION BY CATION EXCHANGE CHROMATOGRAPHY

It is beneficial to collect, concentrate, and purify plutonium from the original nitrate solutions by a simple and efficient technique. Cation exchange chromatography has been used for 30 years on the bench and plant scale to accomplish this task. Cation exchange is internationally recognized as a simple and efficient method for accomplishing this task.

If organic cation resins were totally stable and not susceptible to chemical and/or radiolytic damage, there would not be a need for further evaluation or development. Since such is not the case it is important that we understand the degradation phenomena and also test and/or develop alternate ion exchangers that are less susceptible to chemical or radiolytic degradation.

Inorganic ion exchangers are much more stable than organic ion exchangers and are therefore inherently safer to use. Various inorganic exchangers have been tested but have failed to displace organic cation ion exchangers because they have exhibited significantly less ion exchange capacity than organic ion exchangers. The purpose of this test plan is to

synthesize two new inorganic ion exchangers titanium antimonate and stannous antimonate, and to test their exchange capacity and stability against HCR-S (a standard organic cation exchanger).

Organic resins are not immune from chemical or radiolytic degradation. The results of such degradation is to

- Delink the 3-dimensional matrix through bond rupture at the methylene sites
- Add hydroxyl groups to the resin at the site of ruptured bonds.
- Defunctionalize as the active functional group is reacted. This results in lowering of 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 ion exchange resins, none have exhaustively studied these phenomena over time so that the operational lifetimes can be adequately predicted. The intent of this test plan is to define the operational life of the resins when degraded over time.

3.0 TEST ITEMS

Cation Exchange Materials include:

- Titanium antimonates
- Stannic antimonates
- HCR-S cation exchange resin.

4.0 GENERAL DESCRIPTION OF TESTS

Titanium and stannic antimonates will be synthesized. These materials and HCR-S cation exchange resin will be tested to determine the distribution and selectivity coefficients, and ion exchange capacity of each material. The ion exchange capacity, and thermal stability of these materials also will be correlated to the natural alpha radiation dose, hydrogen ion activity, nitrate ion activity, and exposure time. These tests may be divided into two sections.

1. **Batch Experiments.** Sixteen experiments will be run for each cation 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 10.0 will be conducted in 1-L sealable glass vessels. Because two inorganic and one organic ion exchanger are being tested, this will result in 48 batch experiments. Once each month, 5 grams of resin will be withdrawn and tested for ion exchange capacity and thermal stability.
2. **Column Experiments.** All ion exchange materials will be tested (in duplicate column experiments) to determine 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. Monthly, a 3-gram resin sample will be removed and tested for distribution coefficients, ion selectivities, ion exchange capacity and thermal stability.

5.0 TEST CONDITION LIMITS

Cation exchange batch and column experiments will be performed at room temperature. Tests will be limited to 2 years duration. Individual samples of each experiment will be obtained as a function of time and these milligram scale samples will be heated up to 360 °C. in a TGA-DTA instrument to study the thermal stability of these resins.

6.0 INSTRUMENTS AND CALIBRATIONS

Instruments include:

- Packard liquid scintillation counter
- DTA-TGA instrument
- Induction coupled plasma (ICP) instrument
- Ion chromatograph instrument.

Calibration of these instruments is performed on a schedule and in accordance with approved procedures.

7.0 FACILITIES, EQUIPMENT, AND MATERIALS TO BE USED

7.1 FACILITIES

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

7.2 EQUIPMENT REQUIRED

The required equipment include:

- 64 1-L sealable glass vessels
- 6 glass chromatographic columns
- Ionic potential recorder
- Titration burettes.

7.3 MATERIALS

Materials include:

- Deionized water
- $\text{Pu}(\text{NO}_3)_4$ storage solutions
- Cation exchange materials
- Ultima gold cocktail

- Laboratory reagents such as antimony pentachloride (SbCl_5) Stannic chloride (SnCl_4), titanium chloride (TiCl_4), aluminum nitrate $\text{Al}(\text{NO}_3)_3$, nitric acid (HNO_3), and sodium hydroxide (NaOH).

8.0 SAFETY

8.1 CRITICALITY SAFETY AND RADIOLOGICAL SAFETY

Safety considerations include both criticality and radiological safety. Both are important to glovebox and open-faced hood operations. These will be assured by rigid adherence to CPS-L-114-00010, -00020, -00030, -00040, and -01900 and to the building Radiation Work Permits (RWPs).

8.2 HANDLING CHEMICALS

All chemicals will be handled in accordance with the WHC Chemical Hygiene Plan (WHC-SD-CP-HSP-001) and in accordance with the specific instructions contained in the Appendix Section 17.2.

8.3 REAGENT CHEMICAL SAFETY

See Section 17.3 in 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:

$$K_d = \frac{\text{TRU element activity in exchanger (mmol/g)}}{\text{TRU element activity in solution (mmol/g)}}$$

The distribution coefficients will be determined for each of these exchange materials as a function of the nitric acid activity and as a function of the solution ionic strength.

10.2 SELECTIVITY COEFFICIENT

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

The selectivity coefficient will be measured for the TRU elements and for common contaminants such as sodium, calcium, iron, aluminum, gallium, and rare earths.

10.3 ION EXCHANGE CAPACITY

The ion exchange capacity of these materials 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 7 molar and conc. HNO_3) will be measured. Independent parameters for these tests will include:

- Absorbed alpha radiation dose
- Hydrogen ion activity
- Nitrate ion activity
- Exposure time.

10.5 CHEMICAL STABILITY

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

Table 1-1. Independent Variables for Resin Degradation.

Independent variable	Low setting	High setting
Plutonium loading	10% saturation	Saturation
Hydrogen ion Activity	0.5 molar	3 molar
Nitrate ion activity	0.5 molar	7 molar
Time months	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 materials in response to the number of months of continuous and typical use. This measures the response of the material to dynamic flow conditions, load and unload cycles, and changing chemical environments. The material will be sampled on a monthly basis and the sampling program will continue for a two-year period.

11.0 PERSONNEL REQUIRED

Only normal Plutonium Process Support Laboratory personnel are required.

12.0 WITNESSES REQUIRED

None are required. Nuclear Safety and the PFP Criticality representative will witness the tests.

13.0 PROCEDURE FOR TESTS

13.1 PROCEDURE FOR SYNTHESIZING THE INORGANIC ION EXCHANGE MATERIALS

1. **Tin (IV) Antimonate (SnSbA).** Eight molar antimony pentachloride and 8 molar stannic chloride react vigorously with water and are therefore prehydrolyzed by the following technique. Prehydrolysis is performed in a "cold" sash hood in room 191 by adding the metal chlorides dropwise to an equal volume of chilled water. The slow addition rate and tiny reaction mass assure the safe conversion of the metal chlorides to the hydroxide form. HCl product gas is scrubbed in a sodium hydroxide trap before the off-gas is released to the E-3 ventilation system. An aliquot of 4M antimony pentachloride ($SbCl_5$) is mixed with a requisite amount of 4 M $SnCl_4$ solution at 60 °C. The mixed solution is then poured into a 25 fold volume of deionized water at 60 °C to form a precipitate. The precipitate is aged in the mother solution for 4 days followed by thorough washing with deionized water to remove a large part of the resultant HCl until the pH > 1.5. The washed product is dried at 60 °C, ground, and sieved to obtain a 100-200 mesh-sized fraction.
2. **Titanium (IV) Antimonate (TiSbA).** An aliquot of 4 M $SbCl_5$ is added to a requisite amount of 4 M $TiCl_4$ solution prepared by pre-hydrolysis of liquid $TiCl_4$. The mixed solution is then poured into a 25 fold volume of deionized water at 60 °C to form the precipitate. The product is aged for 4 days, washed and dried as in the above procedure.

13.2 PROCEDURE FOR DETERMINING THE DISTRIBUTION COEFFICIENT

For each of the exchanger materials, 0.2 grams in the H^+ form will be equilibrated with 20 cm³ of the mixed solution containing a TRU element and HNO_3 with intermittent stirring at 25 °C. Am-241 will be determined by gamma counting, and 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 nonradioactive elements will be determined by spectral adsorption such as ICP.

13.3 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 H+ will also be measured in both the aqueous and ion exchange materials. This will allow a comparison between the affinity of the given cation and the affinity of hydrogen ion for the exchange material as in the equation:

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

where:

X_M^* = the ionic fraction of metal ion in the exchanger material

X_H^{*n} = the ionic fraction of hydrogen in the exchanger material raised to the nth power.

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

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

γ_H^n = The activity coefficient of hydrogen in the aqueous solution raised to the nth power

γ_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 since the distribution coefficient is an empirical factor that cannot be correlated to the remaining system parameters whereas the selectivity coefficient can as in:

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

where C has a negative value and is called the Kielland coefficient. The absolute value of C is small for organic ion exchangers but is quite large for most inorganic ion exchangers.

13.4 PROCEDURE FOR THE PARAMETRIC STUDY

For each ion exchanger type, 16 parametric experiments shall be performed. Each experiment shall consist of first determining the chloride ion exchange capacity of the material. Then 300 grams of the material 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 material will be tested for thermal stability and ion exchange capacity as a function of time.

Thermal stability will be tested using a DTA-TGA. Heat flow to or from the sample will be determined as a function of reaction temperature using DTA techniques. 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 monthly for 2 years.

The results of the DTA-TGA tests are considered highly accurate. A one sigma deviation of test results fall within 1% of the measured value.

For the processing tests using 10-L and product receiving can solutions, extraction, concentration, and purification of plutonium shall be accomplished using a standard laboratory procedure for cation exchange. This procedure is included as Appendix 17.

14.0 DISPOSITION OF TEST ITEMS REQUIRED

Plutonium nitrate shall be converted as a minimum to stable oxide. Preferably pressed and sintered PuO₂ pellets shall be stored in the vaults. All aqueous waste materials shall be discharged to tank farms. Resin residues shall be ashed, leached, 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.

17.0 APPENDIX A

17.1 STANDARD LABORATORY PROCEDURES

Cation Exchange Column Experiments

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

Resin Preparation. HCR-S cation exchange resin shall be used as one of the solid phase chromatographants. 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 the solid beads have settled and the broken fragments are still in suspension. This process is repeated a second time. The resin is suspended in water and transferred to the column making sure that an excess of water covers the resin at all times.

Resin Conditioning. The resin is conditioned with 2-column volumes of 3.5 M HNO_3 (prepared by diluting 225 ml of con. HNO_3 into 1 L of distilled water). The flow rate is adjusted to not exceed 5 ml/per 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 adjusted 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. The final hydrogen ion concentration must be maintained above 1.0 molar to prevent the formation of plutonium polymer.

Valence Adjustment. To absorb efficiently, plutonium must be in the +4 oxidation state. If plutonium (V) or plutonium (VI) is in the feed stream, reduction to plutonium (III) can be accomplished by using a reductant such as the ferrous ion or hydrogen peroxide. The concentration of penta or hexavalent plutonium for each feed solution will be determined spectrophotometrically. After adjusting the reductant/ $\text{Pu}^{+5,+6}$ ratio to the stoichiometric point plus 10%, 10 grams/liter of sodium nitrite is added to stabilize $\text{Pu}(4)$, and the solution is heated to 80 °C. for 1 hour to allow the nitric acid to oxidize plutonium (III) to plutonium (IV).

Loading the Column. The filtrate may be added to the column and loaded at the rate of 5 ml/min. Plutonium will load as a colored band and this band can be tracked visually as the column progressively loads and is eventually stripped. The column should never be loaded or left in contact with strong acid.

Stripping the Column. After loading, the column should be washed with 2-column volumes of 1 M nitric acid to remove all contaminants and then eluted with 3-column volumes of 3 M HNO_3 (prepared by diluting 190 ml of con HNO_3 into 1-L distilled water).

Storage Conditions. After stripping, the column can be stored in 0.5 M HNO_3 . After use, the column should be stored with at least 3 in. of fluid over the resin to ensure the stability of the resin bed and to prevent air entering the column. If air does enter the column, the resin must be reslurried to expel the air before reuse.

17.2 STANDARD LABORATORY MATERIAL HANDLING PROCEDURES

Acids or Strong Bases

Clothing Requirements include

- Coveralls
- Rubber or plastic apron
- Rubber gloves
- Face shield or safety goggles
- Shoes with non-skid soles
- Reagent bottles to be in an approved carrier.

Ventilation Requirements. All acids or strong bases will be mixed or reacted in a glovebox or an open-faced hood.

Transportation and Use. Concentrated acids or bases must be transported to an open-faced hood or glovebox 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 this work plan. Care must be exercised to prevent the external or internal contamination of persons with concentrated acids or bases.

Dilution Procedure

- Affix oxidizer/acid or base labels to plastic bottles
- Don clothing, acid apron, rubber gloves, and face shield or safety goggles
- Place H₂O in volumetric flask
- Add conc. acid or base
- Dilute to volume
- Invert and shake 10 times
- 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.

Dry Chemicals

Ventilation Requirements. All handling and reactions must be performed in a glovebox or an open-faced hood.

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

Eye Protection. Chemical safety goggles or glasses shall be worn when handling strong acids or bases.

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 which is not contained in a sealed canister, or confinement device such as a glovebox or an open-faced hood. Rubber gloves shall always be worn to protect the hands.

Ventilation Requirements. All handling and reactions must be performed in a glovebox or an open-faced 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. Call 911 for medical attention immediately.

Skin Contact. Remove contaminated clothing and shoes immediately. Wash 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 15-20 min): Continue irrigating and call 911 for immediate medical assistance.

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

17.3 CHEMICAL REAGENT SAFETY

The following information was compiled from individual MSDS's, Sax's book "The Dangerous Properties of Industrial Materials", and several other sources. Future information may become available during the course of these experiments and these sources should be consulted regularly as revisions become available.

17.31 NITRIC ACID (MSDS 1384)

Chemical Formula - HNO_3

Synonyms. Aqua Fortis; Azotic Acid; Hydrogen Nitrate; Nitryl Hydroxide; Nital.

Properties. Clear to yellowish liquid.

- M.P. -42 °C.
- B.P. 83 °C.
- Density 1.503 g/cc

General Description. Nitric acid is flammable by chemical reaction with most organics and other reducing agents; it 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, it emits highly toxic fumes of NO_x 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 immediate emergency assistance.

Medical Description. Nitric acid is a human poison by unspecified routes; an experimental teratogen (damages DNA). It contains experimental reproductive effects. It is corrosive to eyes, skin, mucous membranes and teeth. It may cause upper respiratory irritation that 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.

17.32 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 form, it is a clear liquid; it may be viscous if concentrated.

- M.P. 159 °C
- B.P. 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 on 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 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 severe pneumonitis.

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

17.33 ULTIMA GOLD COCKTAIL (MSDS #21700)

Chemical Formula - Mixture or 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 alkyl-naphthalene with scintillators PPO and bis-MSB and emulsifiers. Contains a mildly irritating solvent alkyl-naphthalene. 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.

17.34 ANTIMONY PENTACHLORIDE - MSDS #1922

Chemical Formula - SbCl_5

Synonyms. Antimonic Chloride; Antimony perchloride; Antimony (V) Chloride.

Properties. Colorless to red-yellow oily liquid.

- M.P. $-3.5\text{ }^\circ\text{C}$.
- B.P. - Decomposes
- Density - 2.3 g/cc

General Description. Reported in EPA TSCA Inventory. Antimony and its compounds are classified as a corrosive material and is poisonous by ingestion. When exposed to water, it hydrolyzes to Sb_2O_5 and emits fumes of HCl . When heated to decomposition it emits toxic fumes of chloride and Sb.

First Aid Instructions. For external contamination, follow standard laboratory procedures for by flushing external skin and clothes with water. For ingestion call 811 for emergency assistance.

17.35 TITANIUM TETRACHLORIDE

Chemical Formula - TiCl_4

Synonyms. Titanium Chloride.

Molecular Wt. 189.70

Properties.

- Colorless liquid
- M.P. $-24.1\text{ }^\circ\text{C}$
- B.P. $136.4\text{ }^\circ\text{C}$
- Density 1.73 g/cc

General Description. Titanium chloride possesses a penetrating acid odor and is an irritant to the eyes and respiratory tract. It absorbs moisture from air evolving dense white fumes. It is on the EPA Extremely Hazardous Substance List and is on the community right to know list. It is classified as a corrosive material and is poisonous by inhalation. When exposed to water, TiCl_4 hydrolyzes to $\text{Ti}(\text{OH})_4$ and emits fumes of HCl ; when heated to decomposition it emits toxic fumes of chlorine.

First Aid Instructions. For external contamination, follow standard laboratory procedures for by flushing external skin and clothes with water. For ingestion call 811 for emergency assistance.

17.36 STANNIC TETRACHLORIDE - MSDS #2062

Chemical Formula - SnCl_4

Synonyms. Tin Tetrachloride; Tin (IV) Chloride.

Molecular Wt - 260.53

Properties. Fuming caustic liquid.

- M.P. $-33\text{ }^\circ\text{C}$
- B.P. $114\text{ }^\circ\text{C}$
- Density 2.26 g/cc

General Description. Tin chloride is highly irritating to the eyes and respiratory tract; absorbs moisture from air evolving dense white fumes. When exposed to water, it hydrolyzes to $\text{Sn}(\text{OH})_4$ and emits fumes of HCl. As the pentahydrate, it forms white or slightly yellow crystals or fused small lumps; with a slight HCL odor.

First Aid Instruction. For external contamination, follow standard laboratory procedures for by flushing external skin and clothes with water. For ingestion call 811 for emergency assistance.

17.37 HCR-S CATION EXCHANGE RESIN MSDS #25894

Chemical Formula - $(\text{C}_8\text{H}_9\text{N}^+)_x$

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 cation exchange resin is a high molecular weight styrene divinylbenzene polymer that has been sulfonated to form an exchange site. At room temperature it is considered a chemically stable organic compound with a low vapor pressure. At elevated temperatures (> 204 °C.) decomposition occurs.

17.38 SAFELY USING CATION 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. In an unconfined state, in contact with a strong oxidizer, and at the deflagration temperature, they simply burn.

When confined, 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 ion exchange resins are as follows:

- The first safety measure is to prevent degradation; (since most resin accidents involve degraded resins). Degradation may be prevented by:
 - Minimizing the concentration of strong oxidizers that contact the resins. The maximum nitric acid concentration used in an operating column will be 7 Molar.
 - Minimizing the time allowed for strong oxidizers on the column. The nitrate concentration in stored columns will not exceed 1/2 molar.
 - Minimizing the integrated radiation dose absorbed by the resin. Resins are typically considered completely degraded when the integrated radiation dose exceeds 5×10^8 rads. Consequently the radiation dose on operating columns will be limited to 5×10^6 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.
- The third safety measure is to design the columns with large openings or pressure relief plugs so that if a pressure excursion occurs, most of the resin is ejected to an unconfined state. 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.

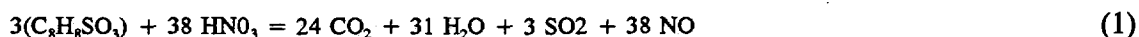
The necessary periodicity for change is a function of the total exposure to oxidizers and radioactivity integrated over time.

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 that could be released if an exothermic excursion occurs.

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



The heat of reaction is calculated as follows:

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

$$H_{\text{CO}_2} = -94.05 \text{ Kcal/mole}$$

$$H_{\text{H}_2\text{O}} = -57.80$$

$$H_{\text{SO}_2} = -75.95$$

$$H_{\text{NO}} = +21.56$$

$$H_{\text{C}_8\text{H}_8\text{SO}_3} = -181(\text{est.})$$

$$H_{\text{HNO}_3} = -49.37$$

$$H_r = \{[24(-94.05) + 31(-57.8) + 3(-75.95) + 38(21.56)] \\ - [3(-181) + 38(-49.37)]\}$$

$$H_r = -1038.51 \text{ kcal/3 mole}$$

$$= -346.17 \text{ kcal/mole}$$

This heat will be absorbed by the glovebox structure, the atmosphere in the glovebox, by the aqueous phase in the ion exchange column, and by converting some of the liquid water to water vapor.

The total volume of the glovebox 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,

$$\begin{aligned} M_{\text{H}_2\text{O}} &= 60 \text{ cm} \times 3.1412 \times (1.25 \text{ cm})^2 / 18 \text{ cm}^3/\text{mole} \\ &= 16.36 \text{ moles liquid water} \end{aligned} \quad (4)$$

The heat absorbed by the liquid water is given by:

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

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.

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

the liquid water which changes to a vapor absorbs heat

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

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

Now three independent variables are contained in equation 8:

- The number of moles of resin M_{resin}
- The equilibrium temperature T
- The number of moles of steam M_{steam}

A value is assigned to M_{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_{steam} in equation 7. After a few iterations convergence is achieved.

This calculation was performed with the Mathematica software program and 2.55 moles of resin may be oxidized instantaneously to bring the glovebox up to its allowed overpressure limit of 10 lb/in².

This calculation represents an extreme limiting case because we have assumed that oxidation is both complete and instantaneous. In actual fact an open 2-inch 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 glovebox surfaces.

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