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AEC RESEARCH AND DEVELOPMENT REPORT

CURIUM PROCESS DEVELOPMENT

III-4. EVALUATION OF POTENTIAL HAZARDS FROM CHLORINATION OF AMINES AND AMMONIA

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by

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ABSTRACT

Studies of the three solvent extraction steps involving a chloride matrix and of the americium-curium hydroxide precipitation step of the Savannah River ^{244}Cm process show that no hazards exist from the formation and accumulation of chloramines. Both alkyl and inorganic chloramines are unstable under process conditions, and were not detected in process solutions.

FOREWORD

This report is one in a series that describes the development of separations processes for purifying ^{244}Cm produced in Savannah River reactors. The series is being issued under the general title Curium Process Development. Following the general title, a roman numeral designates the subject area of the report, and an arabic numeral designates the series report number in that subject area. A subtitle describes the content of each report. Subject areas foreseen for this series are:

I. General Process Description
II. Chemical Processing Steps
III. Analytical Chemistry Support

Reports issued in this series include:

I. General Process Description by I. D. Eubanks and G. A. Burney (USAEC Report DP-1009).

II-1. Separation of Americium from Curium by Precipitation of $K_3AmO_2(CO_3)_2$ by G. A. Burney (USAEC Report DP-1109).

III-1. Analytical Techniques for Characterizing Solvent by R. Narvaez (USAEC Report DP-1010).

III-2. Identification of Solvent Degradation Products by D. L. West and R. Narvaez (USAEC Report DP-1016).

III-3. Analytical Control by E. K. Dukes (USAEC Report DP-1039).

CONTENTS

INTRODUCTION

The Savannah River program for producing ^{244}Cm includes the development of separations processes for the purification of the ^{244}Cm produced in Savannah River reactors.(1) The process, which is described in Appendix A, includes three cycles of solvent extraction in a chloride system to separate mixed americium-curium from fission products and ^{252}Cf, and also precipitation and calcination steps to separate americium from curium and to form americium and curium oxides.

A test tube explosion in the course of process development prompted a study of the possible hazards from chlorination of nitrogen compounds during the solvent extraction and the hydroxide precipitation steps. The explosion and its probable cause are described in Appendix B.

In the solvent extraction steps, the organic solvent (a 30 vol % tertiary octyl and decyl amine mixture in diethylbenzene) is contacted with concentrated aqueous chloride solution. The process solutions are subjected unavoidably to intense alpha radiation (up to $\sim 5 \times 10^{11}$ dis/min/ml) emitted by curium and other radioactive elements. Radiolytically generated chlorine could react with the tertiary amine or the amine degradation products to form alkylchloramines.(2) Although little information on the properties of alkylchloramines is reported, all compounds containing a nitrogen-chlorine bond are quite reactive, and alkylchloramines may react with explosive violence under some conditions.(3,4)

In the hydroxide precipitation step, in which americium and curium are precipitated from a chloride solution by ammonium hydroxide, radiolytically generated Cl_2, Cl atoms, or OCl^- could possibly react with the NH_3 or NH_4^+ to form the inorganic chloramines, H_2NCl, $HNCl_2$, or NCl_3. These chloramine compounds are highly reactive, and NCl_3 is a powerful and unpredictable explosive.

SUMMARY

Studies of the Savannah River ^{244}Cm process showed that no hazards exist from the formation or accumulation of chloramines. The three solvent extraction steps take place in an acidic medium in which chloramines form slowly and rapidly decompose. In two of the solvent extraction steps (lanthanide removal and californium rejection), the medium is also reducing which further prohibits the formation and accumulation of chloramines. Furthermore, no evidence was found that either N,N-dichloro-n-octylamine

or N-chloro-di-n-octylamine (two of the compounds most likely to be formed) is explosive under the conditions required for solvent extraction. In the ammonium hydroxide precipitation step, inorganic chloramines were not detected. Apparently, no significant quantity of chloramine precursors (Cl_2, Cl atoms, or OCl^-) are produced in the alkaline solution during precipitation of the actinide hydroxides.

DISCUSSION

CHLORINATION OF AMINES

The solvent in the curium process consists of 30 vol % tertiary amine (mainly tri-n-octyl and tri-n-decyl amines) in a diethylbenzene diluent. N,N-dichloro-n-octylamine and N-chloro-di-n-octylamine are representative of the chloramines that might be produced from this solvent and were studied to evaluate potential hazards.

The properties of octylchloramines were not found described in the literature, but the properties of other alkylchloramines are expected to apply as follows.(8-10) In general, alkylchloramines are strong oxidants and in pure form decompose spontaneously (but not violently) between 25 and 40°C. Above 40°C, decomposition is more rapid and may be violent, especially in relatively closed systems as in distillation. In the presence of acids, decomposition is accelerated and yields a variety of products including chlorinated and cyclic compounds. Chloramines are also unstable in the presence of strong bases and undergo rearrangements into such products as nitrites, amides, and acids.

The N,N-dichloro-n-octylamine of 86% purity prepared for this study, as described in Appendix C, was a yellow liquid ($d_{25}^{25} = 1.1$) miscible with common organic solvents but insoluble in water. Analytical methods used in these studies are described in Appendix D. The absorption spectrum of the material in isooctane exhibited a maximum at 3060Å with a molar extinction coefficient of 290. These values are in reasonable agreement with the data reported by Metcalf(8) for C_4 alkylchloramines in water. Differential thermal analysis of the compound showed an exothermic reaction at 145°C. However, the exotherm does not necessarily indicate a violent reaction and can be explained as a cyclization reaction of the Hofmann-Loffler type.(8) The compound decomposed slowly in unacidified process solvent, but decomposed completely (but not violently) within ten seconds in acidified solvent. The decomposition products were not identified, but no compounds containing positive chlorine (e.g., other alkylchloramines or

NCl_3) were detected in the organic or aqueous phases after decomposition.

The pure N-chloro-di-n-octylamine obtained from Chemical Samples Company, as described in Appendix C, was a yellow liquid (d^{25}_{25} = 0.86) miscible with organic solvents but insoluble in water. The absorption spectrum in isooctane showed a maximum at 2750Å with a molar extinction coefficient of 370, in agreement with data by Metcalf.(6) The differential thermal analysis of the compound showed an exothermic reaction at 155°C, which can be explained in the same manner as for the dichloramine. The monochloramine is more stable than the dichloramine; decomposition in unacidified process solvent was very slow, and only 50% was decomposed in 24 hours in acidified solvent. The decomposition products were not identified, but no evidence was found for any new positive chlorine compounds. However, decomposition in acidified solvent was complete within ten seconds in the presence of stannous ion, which is added to the curium process to maintain reducing conditions for lanthanide removal and californium rejection.

Alkylchloramines are concluded not to constitute a hazard in the solvent extraction steps. The acidic and reducing conditions required for lanthanide removal and californium rejection prevent the formation and accumulation of these compounds. Analyses of process solutions from development tests with the miniature mixer-settlers verified the absence of alkylchloramines in these steps under normal conditions. In the nitrate-to-chloride conversion, solvent is contacted with 8M HCl in the absence of a reductant. Assuming a 1-g ^{244}Cm/l feed, a G-value (G = molecules per 100 ev absorbed energy) for Cl_2 generation of 2.5 molecules/100 ev, and the same G-value for alkylchloramine production (by 100% conversion of the Cl_2 to chloramines), the maximum alkylchloramine concentration possible under normal operating conditions is 0.01M. Because conditions are unfavorable for formation of alkylchloramines and even less favorable (high acidity) for stability, no significant buildup of alkylchloramines is expected in the nitrate-to-chloride conversion. A process upset resulting in oxidizing conditions in a static system would permit formation of alkylchloramines; the consequences, however, should not be serious because the compounds, although reactive, on the basis of experimental evidence do not appear to be explosive. Furthermore, any accumulation of chloramines can be destroyed by addition of a suitable reductant.

CHLORINATION OF AMMONIA

In the hydroxide precipitation step of the curium process, a solution of americium and curium in hydrochloric acid is added to an excess of concentrated (15M) ammonium hydroxide. Inorganic chloramines could possibly be formed in this step if Cl_2, Cl atoms, or OCl^- ions were generated radiolytically and reacted with NH_3 or NH_4^+. The main product of this reaction sequence is reported to be NH_2Cl at pH >5; $NHCl_2$ is formed between pH 3 and 8 but is unstable in aqueous solutions; and NCl_3 is formed only in acid solutions (pH <3).(11) A precipitation test at 3% of process scale was conducted to evaluate the potential hazards of these chloramines.

In the test precipitation, a solution containing 10 g $^{243}Am^{3+}$/l and 10 g $^{244}Cm^{3+}$/l in 6M HCl was added during ~30 minutes to an excess of 14.8M NH_4OH at 35°C. (The feed solution had been aged for three days before the test to accumulate radiolysis products.) The supernatant solution from the precipitation (~1.4M NH_4OH and ~3.7M NH_4Cl) was sampled for analysis at intervals of 15 minutes, one hour, and four hours after precipitation, and then irregularly during the next eight days. The rate of gas evolution from the slurry of precipitate was measured, and the gas composition was analyzed 40 hours after precipitation, when the solution contained 1M NH_4OH. On the ninth day after precipitation, hydrochloric acid was added to dissolve the slurry and to adjust the HCl concentration to 0.1M; the rate of gas evolution and the gas composition were then determined again.

No NH_2Cl, $NHCl_2$, or NCl_3 was detected by ultraviolet spectrometry in any of the test samples (limit of detection, ~0.001M). However, an unidentified oxidizing substance was formed in the supernatant solution during the first two days after precipitation; its oxidizing strength reached a peak of 0.23N one hour after precipitation and decreased to zero after two days. This substance may have been derived from the <0.01M concentration of nitrate present as an impurity, since the oxidant disappeared when the nitrate was depleted. Ultraviolet spectrometry showed that the oxidant was not H_2O_2, NO_2^-, or OCl^-.

Ammonium hydroxide was depleted radiolytically from the slurry at ~0.15M per day in the 1.4 to 0.15M concentration range, except that the rate was about 30% lower during the first day after precipitation. Control experiments showed that the evaporative loss of NH_4OH was <0.03M per day.

The rate of gas evolution was ~270 cc/(hr)(liter of solution) for both the alkaline slurry and the acidified solution. The gas from the slurry contained 84% H_2, 15% N_2, 0.4% CO_2, <0.5% N_2O,

<0.5% NH_3, and <0.1% O_2; that from the solution contained 83% H_2, 8% N_2, 7.5% O_2, 1.4% N_2O, and 0.3% CO_2. The radiolysis yield for hydrogen, $G(H_2)$, was 1.3, a value typical of dilute aqueous solutions, indicating that most of the radiation interacted with the solution rather than with the precipitate. In the slurry, the loss of hydroxyl ion $G(-OH^-)$ was 0.84, and the yield of nitrogen $G(N_2)$ was 0.23. If the loss of hydroxyl ion is ascribed to ammonia decomposition, the material and redox balances indicate formation of oxidized nitrogenous products. Hydroxylamine and hyponitrite ion are reported as intermediates in the oxidation of ammonia in basic solution,(12) and could be involved.

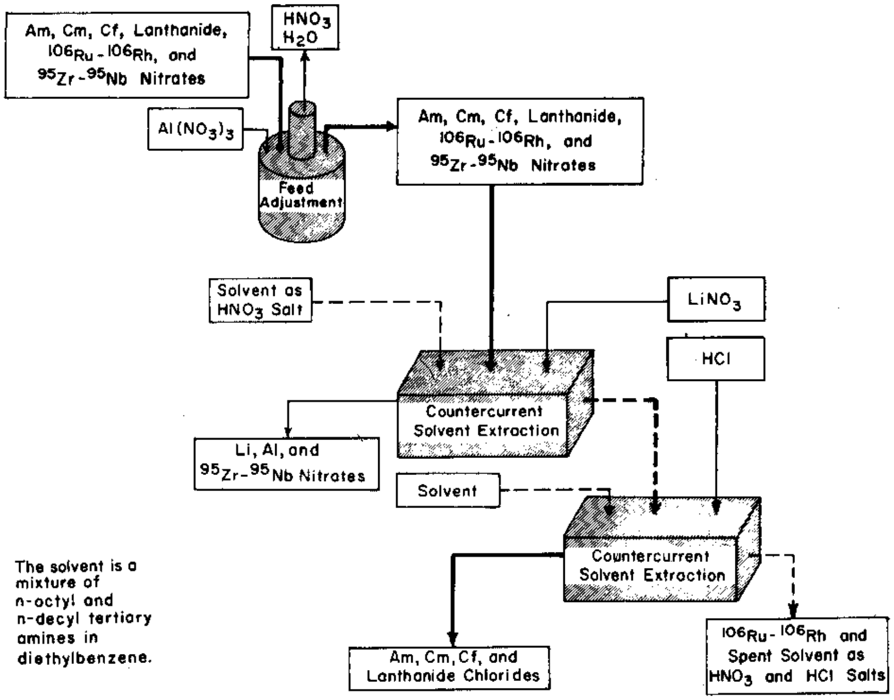
The precipitation of americium and curium hydroxides with ammonium hydroxide is concluded to involve no hazards due to chloramine formation. The absence of chloramines in the process solutions is consistent with gamma radiolysis studies that established that an acidic medium is required for Cl^- to be oxidized to Cl atoms by radiolytically produced OH radicals.(13)

APPENDIX A

THE CURIUM PROCESS

The process for separation of ^{243}Am and ^{244}Cm from rare earths consists of three similar solvent extraction cycles. The first cycle converts from a nitrate system to a chloride system, and the second cycle separates ^{243}Am and ^{244}Cm from rare earths and californium. A third cycle, identical with the second cycle, provides additional decontamination from fission products.

Conditions for the first cycle (conversion cycle) are designed to recover 99.9% of the trivalent actinides and lanthanides in a nitrate-free ($<0.01M\ NO_3^=$) solution of hydrochloric acid (Figure A-1). Trivalent actinides and lanthanides are extracted from an $Al(NO_3)_3$ solution into tertiary amine-HNO_3-diethylbenzene. Good extraction is ensured by controlling the concentrations of Al^{3+}, H^+, and amine. The extract is scrubbed with $LiNO_3$ to remove some of the ^{95}Zr-^{95}Nb and the monovalent and divalent fission products. The actinides and lanthanides are then separated from nitrate by re-extraction into hydrochloric acid. Finally, the hydrochloric acid solution is scrubbed with tertiary amine-HCl-diethylbenzene to remove any residual NO_3^-, Zr, Nb, and Ru.



The solvent is a mixture of n-octyl and n-decyl tertiary amines in diethylbenzene.

FIG. A-1 NITRATE-TO-CHLORIDE CONVERSION

Conditions for the first extraction of the second cycle are designed to obtain yields of at least 99.9% of all transplutonium actinides with decontamination factors greater than 10^4 for removal of the rare earths (Figure A-2). The conditions for the second extraction are designed to provide adequate separation from all fission products that are extracted with americium and curium in the first extraction. The product solution from the first cycle is adjusted with lithium chloride and fed to the second cycle. Americium and curium are extracted into tertiary amine-HCl-diethylbenzene, and the rare earths and residual fission products remain in the aqueous stream. The organic extract is scrubbed with lithium chloride solution to further decontaminate from rare earths. Americium and curium are re-extracted into hydrochloric acid solution, and this solution is scrubbed with tertiary amine-diethylbenzene. Americium and curium are scrubbed in the product stream which is then adjusted for the third cycle. The second cycle can be used to separate californium from americium and curium. If lithium chloride is used instead of hydrochloric acid in the strip solution, californium stays with the fission products in the organic waste.

The third cycle is identical with the second cycle and is necessary to give additional decontamination from cerium.

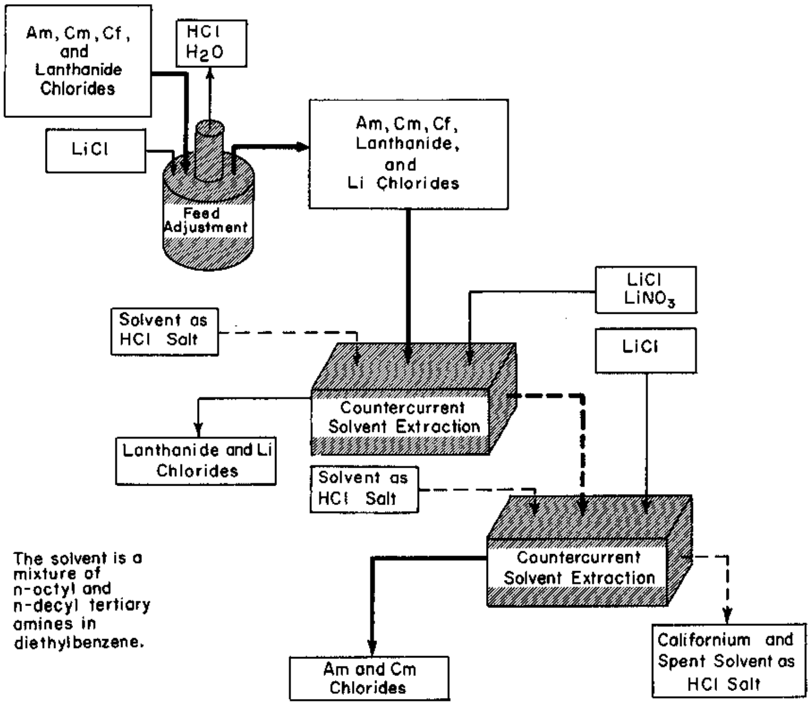


FIG. A-2 LANTHANIDE REMOVAL

The finishing operation (Figure A-3) is designed to yield AmO_2 containing less than 0.5 wt % Cm, and CmO_2 containing less than 0.5 wt % Am. Americium and curium chlorides from the third extraction cycle are concentrated, and americium and curium are precipitated as hydroxides to remove lithium. The precipitate is dissolved to yield a solution containing 50 g/l each of americium and curium in 0.25M HNO_3. After a valence adjustment, potassium carbonate is added to precipitate Am(V). The curium in the supernate then contains less than 0.5 wt % Am. Curium is precipitated as the hydroxide to remove potassium; the hydroxide is dissolved, precipitated as the oxalate, and calcined to CmO_2.

After the carbonate precipitation, the americium precipitate contains 3-5 wt % Cm. A second carbonate precipitation is required to produce americium containing less than 0.5 wt % Cm. The final carbonate precipitate is dissolved and precipitated as hydroxide to remove potassium. The hydroxide is dissolved, precipitated as oxalate, and calcined to AmO_2.

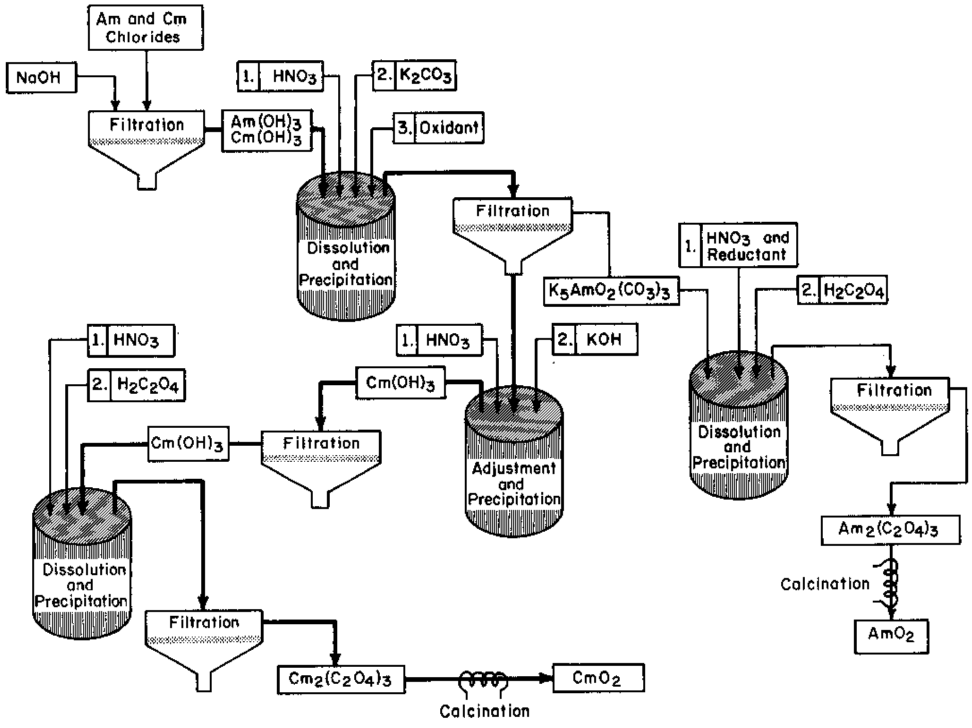


FIG. A-3 REMOVAL OF AMERICIUM AND PREPARATION OF OXIDES

APPENDIX B

EXPLOSION INVOLVING PROCESS SOLVENT

During a weekend, 7 to 10 days after tests of solvent washing procedures, the contents of one stored and capped test tube exploded unexpectedly and damaged three others. The tube in which the explosion occurred contained solvent that had been washed sequentially with aqueous solutions of (1) HCl-Sn(II), (2) HCl-NaOCl, and (3) NaOH; the solvent was stored over the final NaOH solution. The explosion was violent for the relatively small amount of solvent involved (6 ml), but was not a detonation as indicated by the presence of some unpulverized pieces of glass and cap. Explosives experts at Du Pont's Eastern Laboratory advised that the debris was typical of that produced by an overpressurization or explosion in the gas phase.

Several repetitions of the solvent washing tests that led to the explosion were performed under controlled conditions to test for formation or buildup of chloramines or other potentially hazardous compounds. No explosion or other unusual behavior was observed during these experiments, the vessels were not pressurized, and no chloramine compounds accumulated on standing.

Although the actual cause of the explosion remains unknown, the possible involvement of chlorine monoxide is suggested. This compound, which is a gas at room temperature, is a powerful oxidant that may explode spontaneously in the presence of organic materials or when heated or exposed to light.(14) It could be formed by known reactions from chemicals present in the solvent washing system. Hypochlorite ion and gaseous chlorine are related by the acid-base equilibrium

$$\mathrm{OCl^- + Cl^- + 2H^+ \rightleftharpoons Cl_2 + H_2O}$$

Chlorine monoxide can be formed at an intermediate stage in this equilibrium by the reaction:(14)

$$\mathrm{ClO^- + Cl_2 \rightarrow Cl^- + Cl_2O}$$

In the laboratory incident, the intermediate stage of the acid-base equilibrium was present at some time during the washing process, and formation of Cl_2O was thus possible. The Cl_2O would tend to escape from solution and accumulate in the gas phase, where it would be protected by the intervening organic phase from destructive hydrolysis. It should eventually disappear by reaction with organic materials or by decomposition to the elements. The failure to reproduce the explosion in the repeat experiments could perhaps be due to the rather special conditions required to form Cl_2O and to the many complex reactions that lead to its destruction.

Cl_2O conceivably could be formed in curium solutions where strong radiation fields and oxidizing conditions exist. Also, the more explosive compound ClO_2 possibly would be formed under such conditions.(15) However, the reducing conditions specified by the process flowsheet and the ventilation of storage vessels will prevent the accumulation of these materials.

APPENDIX C

SYNTHESIS AND PROCUREMENT OF ALKYLCHLORAMINES

N,N-dichloro-n-octylamine was prepared with a 50% crude yield by the method described by Wright.(7) To a solution of 10.6 g (0.1 mole) of sodium bicarbonate in 60 ml of cold water was added 3.88 g (0.03 mole) of n-octylamine. The mixture was maintained at 6 to 10°C for thirty minutes while chlorine was passed into the stirred mixture. The yellow oil which settled out (density ca. 1.1) was separated and washed successively with cold 2N H_2SO_4, cold water, cold 18N H_2SO_4, and cold water. The resulting oil was filtered through anhydrous calcium chloride. The electropositive chlorine content, as determined by iodometric titration, was 86% of the theoretical value.

Attempts to prepare N-chloro-di-n-octylamine by a modification of the method reported by Coleman(2) resulted in a product that was too impure for storage and use. High-purity N-chloro-di-n-octylamine was purchased from Chemical Samples Company.* This material initially contained 106% of the theoretical electropositive chlorine and was more stable (slower precipitate formation) than the crude material prepared as described above. The purchased material was stored at -78°C until ready for use.

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* Chemical Samples Co., 4692 Kenny Road, Columbus, Ohio 43221

APPENDIX D

ANALYTICAL METHODS

Three analytical methods for chloramines were used in this study: iodometric titration, ultraviolet spectrometry, and thin-layer chromatography. The different techniques were required to avoid interferences.

Iodometric Titration

The oxidizing potential of chloramines in acid solution is due to the electropositive chlorine atom, and is the basis for analysis by iodometry:

$$\mathrm{N{-}Cl} + 2\mathrm{I}^- + \mathrm{H}^+ \rightarrow \mathrm{HN} + \mathrm{I}_2 + \mathrm{Cl}^-$$

The released iodine is titrated with standard thiosulfate. Electropositive chlorine normalities as low as 10^{-3} can be determined. The iodometric titration was used only for samples that did not contain tertiary amines, because tertiary amines complex iodine and therefore mask the end point.

Ultraviolet Spectrometry

The hypochlorite ion and the chloramines soluble in aqueous solution have characteristic absorption maxima for ultraviolet light as shown in Table I, and can be determined by ultraviolet spectrometry at concentrations as low as 10^{-4}M. This technique was most useful for analyzing aqueous solutions from the curium hydroxide precipitation step, but was not used for curium process solvent because of interfering absorption bands from diethylbenzene and the tertiary amine, and because the octylchloramines are insoluble in aqueous reagents.

TABLE I

Ultraviolet Absorption of Chloramines in Water(6)

Chloramine	Absorption Maximum, Å
NH_2Cl	2450
RNHCl	2530
R_2NCl	2630
$NHCl_2$	2970
$RNCl_2$	3030
OCl^-	3100
NCl_3	3400

Thin-Layer Chromatography

A thin-layer chromatography method was developed to determine alkyl N-chloramines in curium solvent, because tertiary amines interfered with both the iodometric and spectrometric methods. Sorption on silica and elution with chloroform resolve the alkyl N-chloramines from interferences. The known R_f ratio (component/solvent travel) is 0.7 for N-mono- and N,N-dichloramine, and is 0.3 for tertiary amines. R_f values for NaOCl and primary and secondary amines are <0.1.

The N-chloramines are detected by spraying the eluted chromatographic plates with an acidic solution of potassium iodide. Although unchlorinated alkylamines produce a faint iodine color, there is no interference because resolution from N-chloramines is complete.

The method is sensitive to ~0.01M N-chloramine in tertiary amine—diethylbenzene solutions, but does not resolve N-monochloramine from N,N-dichloramine.

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